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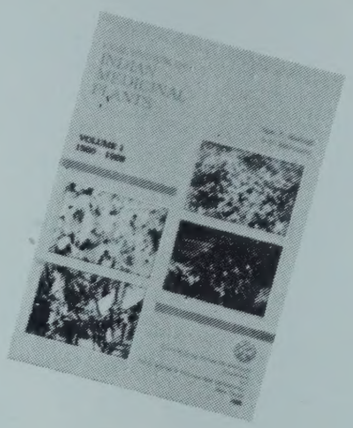
Compendium of Indian Medicinal Plants



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by R P Rastogi and B N Mehrotra

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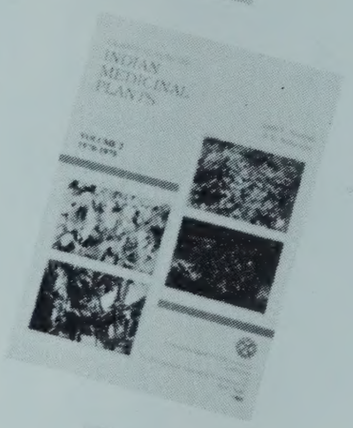

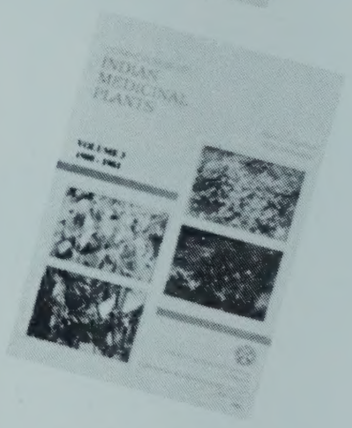

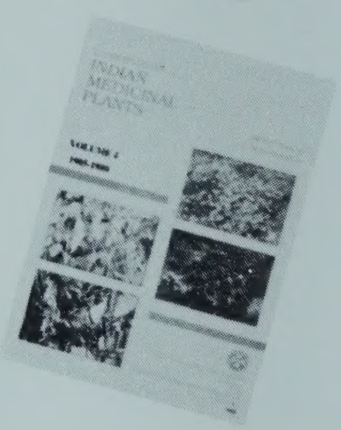

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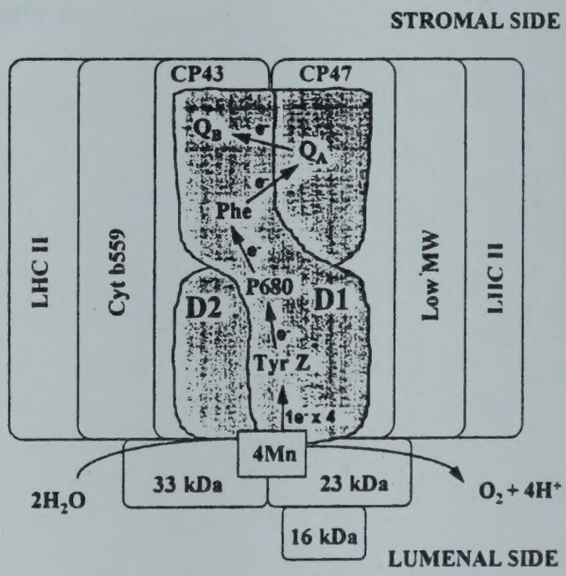

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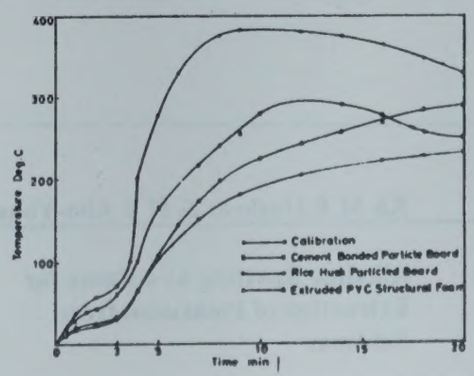

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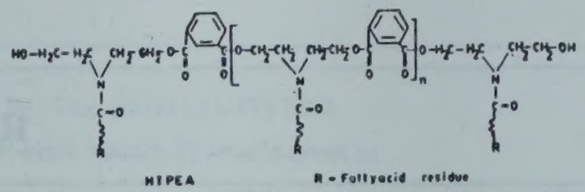

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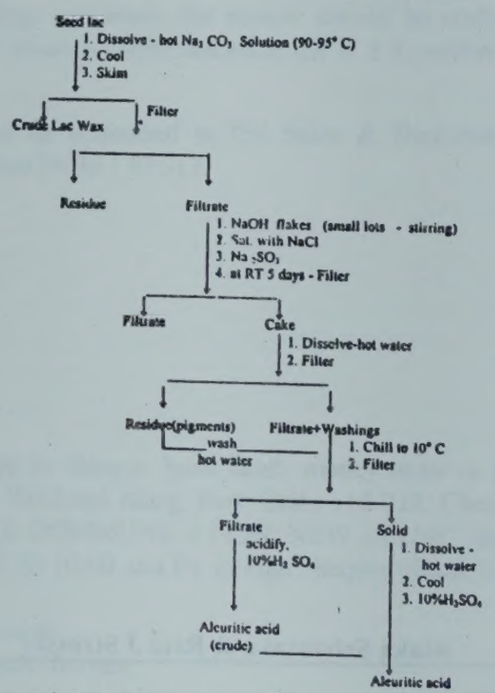

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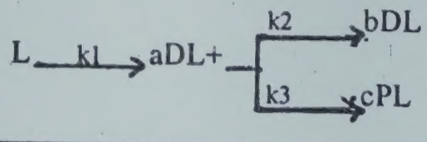

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Constructive and Destructive Actions of Light on the Photosynthetic Apparatus*

Alaka Srivastava[§] and Reto J Strasser

Laboratory of Bioenergetics, University of Geneva, 1254 Jussy- Geneva, Switzerland

Although light is the source of energy for photosynthesis, it can also be harmful to plants. Light as a stressor induces damages which target mainly the photosystem II. Inactivation of electron transport and subsequent oxidative damage of the reaction center may occur. However, light is able to activate special adaptation mechanisms in such a way that the efficiency of the photosynthetic system is optimized and the photodamage is minimized. In this review, different constructive and destructive aspects of light stress are discussed in aquatic and land plants. The response and adaptation of photosynthetic machinery of plants to high light and different environmental perturbations are summarized. In addition, recent advances in understanding the biochemical changes in response to light have been discussed. Different ecophysiological and biochemical protective mechanisms against light stress have also been described.

1 Introduction

It is becoming increasingly evident that changes in the light environment have profound influence on the structure and function of the photosynthetic apparatus. Injury to the photosynthetic apparatus of green plants induced by exposure to strong light has been known for a long time. Damage to the photosynthetic apparatus is caused by wavelengths in the ultraviolet[1,2], by light in the visible part of the spectrum[3-5] and by interaction between visible and ultraviolet light. Various terms have been used to describe the phenomenon of reduction of photosynthetic capacity induced by exposing the organism to light. Some of these terms are photoinhibition, photooxidation, photoinactivation, photoliability, solarization, photodynamic reactions etc. Photoinhibition was initially recognized as a loss of photosynthetic capacity, when plants were exposed to very high light intensities[6,7]. Illumination-dependent losses of photosynthetic electron transport activities have also been recognized for decades as a serious concern in any investigation involving the use of isolated thylakoids[8-10]: among the first physiological analyses of these processes were those of Satoh[11-13] and Björkman *et al.*[14] who compared the sensitivity of thylakoids to photoinhibition using preparations from plants grown under different light regimes. One of the major classical studies were those of Jones and Kok[10]; they did the first systematic analysis.

Green leaves absorb a high portion of the incident visible light. At lower photon flux densities (PFD), an increase in the light intensity will result in an increase in photosynthetic CO_2 fixation. Above a certain PFD, however, photosynthesis saturates and is dependent upon "dark-reactions"; it is incapable of utilizing all the energy absorbed by chlorophyll. In this range of PFDs, various mechanisms operate that protect the photosynthetic apparatus against damage from the accumulation of excessive energy. However, whenever the utilization and dissipation of energy through photosynthesis, in combination with the photoprotective processes, are insufficient for dealing with the absorbed light, the photosynthetic apparatus may be damaged[3,5,15-17]

The extent of photoinhibition varies widely with the physiological state of the plant and external conditions, such as photon flux density and duration of light exposure. Whether excessive light in fact leads to photoinhibition seems to depend on the efficiency

[§]Corresponding author: Dr Alaka Srivastava

*This work is dedicated to Professor Walter Larcher to honor his conceptual ideas about stress as expressed in the title of this review.

of (i) protective mechanism and (ii) recovery and/or repair process.

Several reviews on the responses to plants to high light have appeared. Björkman[18] has reviewed the acclimation that allows a greater capacity for the utilization of high light levels by leaves grown in sun light than by leaves developed under shade. Interest has also been focused on the biochemical basis under which damage can occur[16,19-21]. Some photoprotective responses were considered in the reviews by Powles[3], Demmig-Adams and Adams[5], Krause[22], Baker[4,23], Young and Britton[24], Baker and Bower[25], Chow[26], Demmig-Adams and Adams[27], Demmig-Adams *et al.*[28], Gilmore[29]. This review will focus on recent achievements based on *in vitro* and *in vivo* studies to better understand the process of photoinhibition and photoprotection.

2 Photoinhibition Induced by High Light

Injury to the photosynthetic apparatus of green plants exposed to intense light has been known for a long time. Since there have been several reviews on photoinhibitory damages[3,22,25,26], this topic is discussed with limited number of aquatic and terrestrial plants.

2.1 Aquatic Plants, Algae and Cyanobacteria

Algae are the principle photosynthetic organism in the aquatic environment and their specific response to high light intensities is of primary importance[3,30,31]. Aspects of the physical environment that play a role in photoinhibition include light distribution and water motions, which determine the timing and duration of light exposure. Algal responses to light are also related to the chemistry of natural waters. The distribution of the aquatic photosynthetic organism is limited to the narrow zone of surface illumination, known as the euphotic zone. Photosynthetic organisms exist throughout the entire range of light levels within the euphotic zone[30]. As the fluid environment of the euphotic zone is subject to substantial environmental fluctuation and turbulence motion they often expose organisms to high PFDs. Photoinhibition has been widely observed among natural populations of phytoplankton. Most natural assemblages include both prokaryotic cyanobacteria as well as eukaryotic representatives from the green algae (Chlorophytes), diatoms (Chrysophyte), the dianoflagellates (Pyrrhophytes) as well as other members of the Chrysophyte and Cryptophyte[30].

After high-light exposure, light saturated and light-limited rates of photosynthesis are reduced, indicating effects both on the electron transport capacity and the quantum yield of photosynthesis. Quantum yield of photosynthesis is defined as the moles of O_2 evolved or CO_2 fixed, per mole of photons absorbed; usually it refers to the maximum quantum yield of the process measured at low intensities where the rate of the process increases linearly with increasing number of photons. Laboratory experiments with algae have shown evidence for a primary mechanism of photoinhibition involving interruption of electron transport through PSII[30,32].

Although photosynthetic activity of attached microphytes (seaweeds and sea grasses) and floating seaweeds (e.g. *Sargassum*) has received comparatively less attention than that of microalgae, there are still some studies specifically devoted to photoinhibition[33]. Osmond *et al.*[34] have shown that dissolved inorganic carbon in the sea water protects the marine macroalgae *Ulva rotundata* from excess light. However, prevention of protein synthesis by chloramphenicol and conversion of violaxanthin to zeaxanthin by dithiothreitol (DDT) treatment accelerates photoinhibition[34].

2.2 Terrestrial Plants

Like aquatic plants, land plants occupy a wide range of habitats from extremely shaded environment to fully exposed sun sites. Plants genotypically adapted to open sunny habitats (sun plants) have, in general, the capacity to acclimate and grow in shaded conditions of lower PFD. However, plants genotypically adapted to deeply shaded habitats (shade plants) may not have the ability to acclimate and grow in full sun conditions. The distribution of plants depends in part on adjustments which take place in the photosynthetic apparatus in response to light quantity and morphological responses to light quality[35].

Björkman and Holmgren[6] pioneered experiments with sun and shade plants. They observed that the sun plants growing and photosynthesizing well at higher PFDs were also able to grow, although a bit slowly at low PFD (150 $\mu mol\ m^{-2}s^{-1}$). Shade plants grew very well at low PFD but poorly at higher PFD. Experiments revealed that the quantum yield of pho-

tosynthesis was low when shaded plants were grown at higher PFD. Photooxidative destruction of pigments occurred on exposed parts of the leaves. Experiments with shaded clones of *Solanum dulcamara* showed photoinhibition within minutes of transfer of shade clones from a low to a high PFD[36]. A fern of rain forest also suffers photoinhibition within minutes of transfer to full sunlight conditions[37]. Oberhuber and Bauer[38] have reported that the leaves of *Hedera helix* growing in the shadow of two deciduous trees suffer from photoinhibition of photosynthesis when leaf shading starts in the autumn.

The underlining effects of exposure to higher PFDs have been studied extensively with land plants. After photoinhibition, the electron transport was inhibited which is also evident as changed chlorophyll *a* fluorescence yield. The variable chlorophyll *a* fluorescence at room temperature was lower after exposure to high PFD. A typical Chl *a* fluorescence responses of pea leaves grown in the green house are shown in Fig. 1. Leaf discs were exposed for 20 min to different light intensities, dark adapted for 20 min and then exposed to measuring light of 60 Wm^{-2}. When the Chl *a* fluorescence yield reached to a stable steady state level (F_s), the maximum fluorescence level ($F_m^{\ 1}$) was obtained by giving a short pulse of saturating light (300 Wm^{-2}). Immediately after that the $F_o^{\ 1}$ was measured by simultaneously turning off the measuring light and turning on the far red light. With increasing PFD, a sharp decrease in the Fml was observed. The actual quantum efficiency (ϕ,Po) and maximum quantum efficiency (ϕ, Po) also decreased by increasing the PFD.

In contrast, Björkman and Schäfer[39] observed, with full sunlight grown leaves of cotton, grown under standard furrow irrigation, very high rates of net CO_2 uptake throughout the growing season. Photoinhibitory damage was absent in irrigated cotton grown under normal agricultural practices, even though the solar tracking leaves receive extremely high daily photon irradiances. On other hand, imposition of additive environmental limitations such as water, nutrient or temperature stress further exacerbate the inhibitory effect of a high PFD[3].

There are some plants, however, which can grow in a spectrum of PFD from very low to high. The rainforest tree seedling becomes established under very low PFDs, but as an adult tree, it receives full sunlight on a significant part of the canopy. Experiments have shown that shade plants are more prone to photoinhibition of photosynthesis than are sun

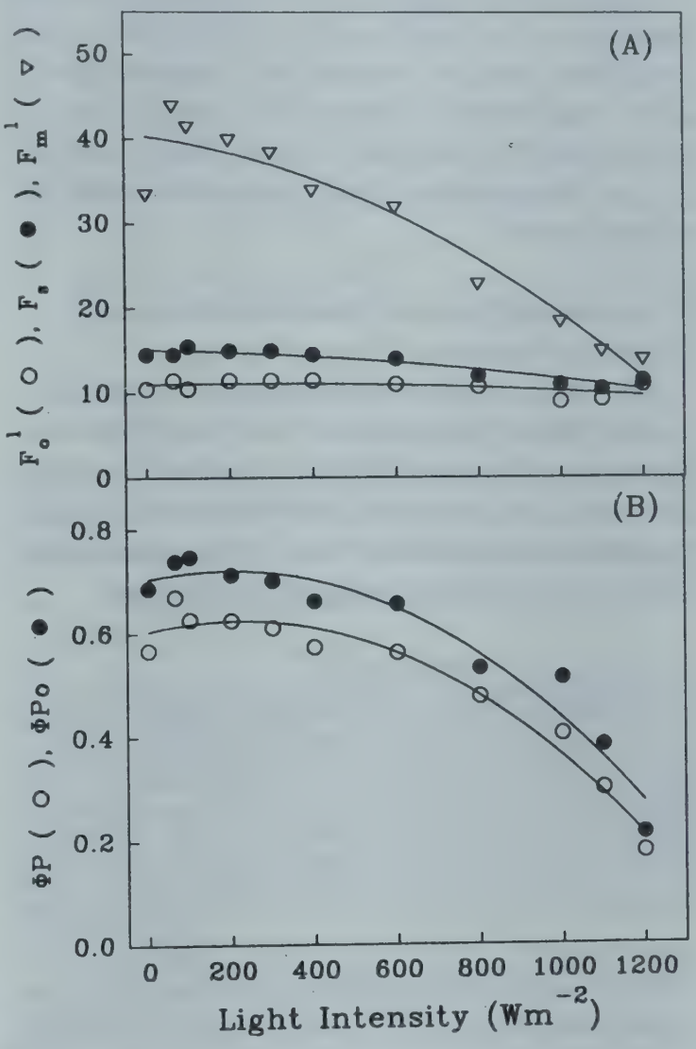

Fig. 1 — Effect of 20 min exposure to different fluence rates of white light on (A) steady state ($F_s^{\ 1}$), maximum ($F_m^{\ 1}$) and minimum ($F_o^{\ 1}$) levels of modulated Chl *a* fluorescence and (B) maximum photochemical efficiency ($\phi Po = 1-F_o^{\ 1}/F_m^{\ 1}$) and actual photochemical efficiency ($\phi P = 1-F_s/F_m^{\ 1}$) of PSII in pea leaves in steady state condition. After the different light treatment, leaves were dark adapted for 20 min at room temperature and then exposed to measuring light (60 Wm^{-2} of blue light (Schott, KL1500 Electronic lamp with a corning filter, CS 4-96)). After few min, the Chl *a* fluorescence yield reached a stable and low steady state level ($F_s^{\ 1}$). The maximum fluorescence level ($F_m^{\ 1}$) was obtained by giving a short pulse of saturating light (blue, 300 Wm^{-2}). Immediately after that the $F_o^{\ 1}$ level was measured by simultaneously turning off the actinic light and turning on the far-red light (Srivastava & Strasser, unpublished results)

plants[3,35]. The higher sensitivity of shade plants to photoinhibition .PA

is generally ascribed to the factors such as a large light absorbing chlorophyll antennae for PSII and lower rate of light saturated photosynthesis[35]. In sun plants, an active repair cycle of PSII replaces photoinhibited reaction centers with photochemically active ones, which confer partial protection against photoinhibition. However, in shade plants, this repair cycle is less pronounced for protection against photoinhibition[40-42].

3 Interaction Between Photoinhibition and Other Environmental Stress Factors

Photoinhibition involves basically the photoinactivation of the photosynthetic machinery. However, the degree of susceptibility is influenced by several factors such as genotypic and environmental factors. The interactive factors between environmental stress and strong light are subsequently highlighted.

3.1 CO_2, O_2, Photoinhibition

Photoinhibition can be strongly affected by the composition of gas phase. Photoinhibition is alleviated by the presence of CO_2 *in vivo*[43-50] or by the addition of bicarbonate *in vitro*[45]. In the absence of CO_2, Eloff *et al.*[46] showed photooxidation of cyanobacteria in natural conditions. In a study with the cyanobacteria, *Spirulina platensis*, Kaplan[47] documented very high photoinhibition when the cyanobacteria were exposed to strong PFD in the absence of CO_2. Exposing an anaerobic photosynthetic bacterium *Chromatium vinosum* to pure oxygen, Asami and Akazawa[48] showed that CO_2 could prevent photoinhibition. On the other hand, Cornic[49] reported that little or no photoinhibition occurred upon the removal of CO_2 from the gas phase surrounding the leaf. This protection was apparently achieved via photorespiratory carbon metabolism fueled by endogenous carbohydrate reserves. The above considerations are supported by numerous experimental studies which suggest that photorespiration serves for disposal of excess photosynthetic energy[50].

The role of O_2 is more complex. In the presence of O_2, the organism can dissipate a part of the excess energy through pseudocyclic electron flow[43,45], or through photorespiration[3,50]. Anaerobic conditions can greatly enhance susceptibility to photoinhibition[51-53]. On the other hand, the presence of O_2 may be required for photoinhibition, since oxygen free-radicals formed by photosynthetic reduction of oxygen[52] may be responsible for the breakdown of the RC II-D1 protein [20,53].

The expected result was observed when the pea leaves were illuminated with photoinhibitory light in air, in air in the absence of CO_2 and pure N_2 (Fig. 2). After 2 h of treatment to 600 Wm^{-2} light intensity, the leaves exposed to N_2 ($-CO_2$, $-O_2$) showed the lowest rate of O_2 evolution or the maximum photodamage. In air the degree of photoinhibition was much lower than that in pure N_2. Insignificant differences in O_2 evolution were observed in the leaves kept in air without O_2 ($+CO_2$, $+N_2$) but the sample kept in air without CO_2 ($+N_2$, $+O_2$) also showed the large photodamage (Fig. 2). These results clearly indicate that: (i) O_2 is an important component to create the photoinhibition in the plants; (ii) in absence of CO_2, photoprotection was achieved via photorespiratory carbon metabolism; (iii) the absence of both CO_2 and O_2 added a synergistic effect which resulted in total damage of the leaves. Similar results were obtained by Gong *et al.*[44] with free floating angiosperm, *Lemna gibba*. After an extensive study with isolated spinach chloroplasts, Godde *et al.*[54] showed that un-

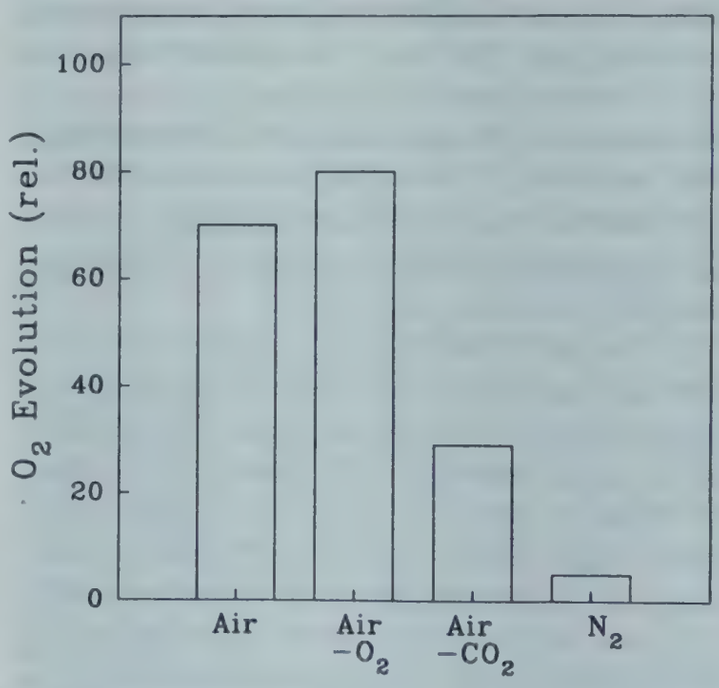

Fig. 2 — Per cent inhibition in O_2 evolution in pea leaves after photoinhibitory treatment in different gaseous atmosphere. Plants were illuminated for 2 h with 700 Wm^{-2} of white light in the atmospheric conditions as indicated and immediately after that O_2 evolution was measured in the air (reproduced the same experiment as Gong *et al.*[44], but with pea leaves)

der nitrogen, high light not only induces photoinactivation of PSII, but also inhibition of PSI.

Photoinhibition has been shown to be associated with partial loss of activity of some of the enzymes of photosynthetic carbon metabolism. Two mesophyll enzymes, NADP-malate dehydrogenate and pyruvate Pi dikinase, showed loss of activity when intact maize leaves were exposed for 3 h to full sunlight without CO[255]. The activity of ribulose 1,5-biphosphate carboxylase-oxygenase has also been found to be reversibly inhibited by exposure of wheat leaves to light without carbon metabolism56.

Molecular oxygen can act as a Hill oxidant. In the Mehler[57] reaction, which is saturated at low O_2 levels, oxygen is reduced by PSI. This reaction seems to provide protection, as seen by the relief of aggravated photoinhibition under anaerobiosis by very low O_2 partial pressures. Reduction of O_2 apparently prevents extreme "over-reduction" of photosynthetic electron carriers and allows the build up of a high proton gradient across the thylakoid membrane that could induce increased dissipation of absorbed light energy as heat. Destructive effects of the superoxide radicals formed in the Mehler reaction may be largely avoided by efficient action of scavenging systems[59].

3.2 Low temperature and Photoinhibition

Exposure of chilling-sensitive plants to chilling temperatures from 0 - 12°C is much more damaging to the photosynthetic apparatus in the light than in darkness. It was also shown that the degree of inhibition increased with increased irradiation and duration of exposure[60a]. Typically, photoinhibition of photosynthesis is manifested as an inhibition of the maximum quantum yield of CO_2 uptake indicating impaired photochemistry. As an example, Fig. 3 shows the rate of O_2 evolution in pea leaves irradiated with 700 Wm^{-2} at 23°C and 3°C. About 20% decrease in O_2 evolution was observed in the plants kept at 23°C for 1 h where as more than 80% of O_2 evolution was lost just after 30 min of exposure at 3°C at the same light intensity.

It is a common feature of all chilling-sensitive plants that their photosynthesis is more susceptible to chilling temperature in light than in darkness[60b]. Neuner and Larcher[61] treated certain soybean cultivars at 0°C for three days and measured the alteration in chlorophyll *a* fluorescence yield. Such alterations

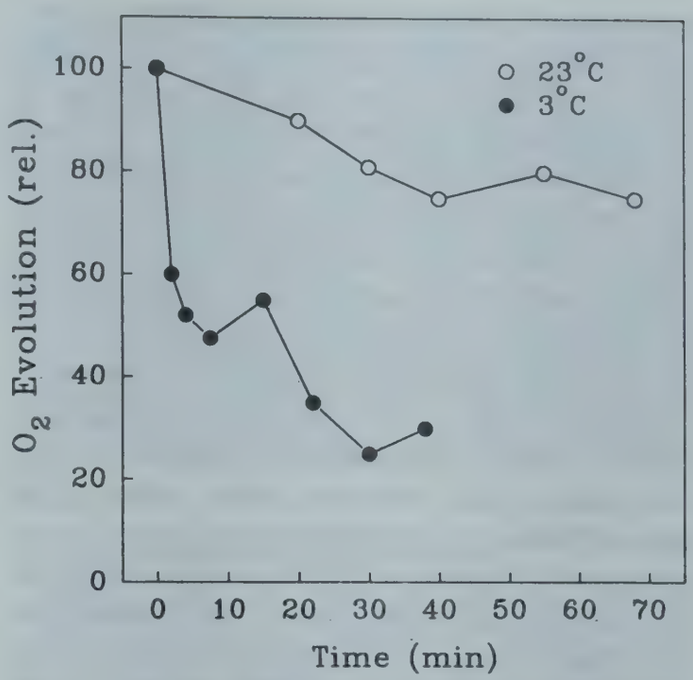

Fig. 3 — Per cent inhibition in O_2 evolution in pea leaves exposed to white light (700 Wm^{-2}) at 23°C and 3°C for different time period (reproduced the same experiment as Havaux and Davaud[60a] but with pea leaves)

were more pronounced with cold treatment under irradiation than in the dark[61]. Hetherington *et al.*[62] have tested more than 15 different tropical and temperate crop species encompassing a wide spectrum of chilling sensitivities. They reached the conclusion that photoinhibition was dependent both on temperature and light.

Chilling in the presence of strong PFD caused substantial loss of PSII fluorescence emission at 77K[63]. Temperature stress also disrupts membrane integrity, so it is possible that chilling in light is associated with increase in leakage of the membranes. This may also be the case for the high temperature[64]. In both the cases, strong light increases the adverse effect of temperature stress and during chilling oxygen contributes to the damage. The adverse effect of oxygen may be the result of generation of singlet oxygen, superoxides or hydroxyl radicals[58,65,66].

Sometime, the plants do get acclimated to both low temperature and high PFD[67-69]. Cold acclimation requires adjustment to a combination of light and low temperature, conditions which are potentially photoinhibitory. The photosynthetic response of plants to low temperature is dependent upon the time of exposure and the developmental history of the leaves. However, the photosynthetic response to low

temperature is clearly species and cultivar dependent[67]. Krause and Somersalo[70] measured the chlorophyll *a* fluorescence induction and quenching at room temperature and 77K in relation to the effects of environmental stresses imposed by chilling in high light and by freezing and thawing the spinach leaves. The data indicate that cold acclimation of spinach plants, which leads to increased frost tolerance of the leaves, results in decreased susceptibility to photoinhibition of photosynthesis at chilling temperature[70]. Evergreen conifers of temperate regions have evolved effective physiological protective mechanism, making them relatively stress resistant, and allowing them to maintain functional foliage for several years[71]. Gombos *et al.*[72] have demonstrated in the cyanobacterium *Synechocystis* that photoinhibition of photosynthesis at low temperature is tolerated by the cells as a result of unsaturation of glycerolipids of thylakoid membranes. In some cases, the plants have developed physiological adaptations, such as to limit water loss, scavenging system to remove reactive oxygen species and protection of membrane and proteins from extreme temperature or desiccation[73].

3.3 High Temperature and Photoinhibition

Like other environmental stresses, high temperature has the potential to predispose chlorophyllous tissues to injury by excess light. As temperature rises above an optimum, photosynthesis begins to decline, at first gradually and reversibly, and then steeply and irreversibly at some critical temperature. Prolonged exposure results in photooxidative destruction of chlorophyll and cell death and especially if photosynthesis is inhibited[3,74,75]. Srivastava and Strasser[76] have reported enhanced photoinhibition when pea leaves were treated with higher temperatures (40°C) and illuminated with 750 Wm^{-2} (Fig. 4).

Contrary to the notion that light would exaggerate the adverse effect of high temperature, it has been reported that light during brief high temperature treatment is beneficial. A series of experiments on heat and light interaction have been done on pea leaves[77-79]. Chlorophyll *a* fluorescence measurements reveal that low light protects against the heat treatment. For example, as shown in Fig. 4, when the pea leaves were exposed to higher temperature in the presence of low light (30 Wm^{-2}) insignificant differences in ϕPo and ϕPo were observed when the leaves were heated for 30 min up to 40°C. It is important to note that this protective effect of light was saturated by a PFD of only 25 Wm^{-2}.

Preheat treatment in the presence of low light (30°C together with 30 Wm^{-2} for 30 min) resulted as well in the protection of the photosynthetic mechanism in samples exposed to high light[79]. Data obtained from the Chl *a* fluorescence induction curves (Fig. 5) show that about 55% decrease in the variable Chl *a* fluorescence was observed when the leaf discs were exposed directly to 750 Wm^{-2} (curve d) for 15 min in comparison to 22% when the leaf discs were

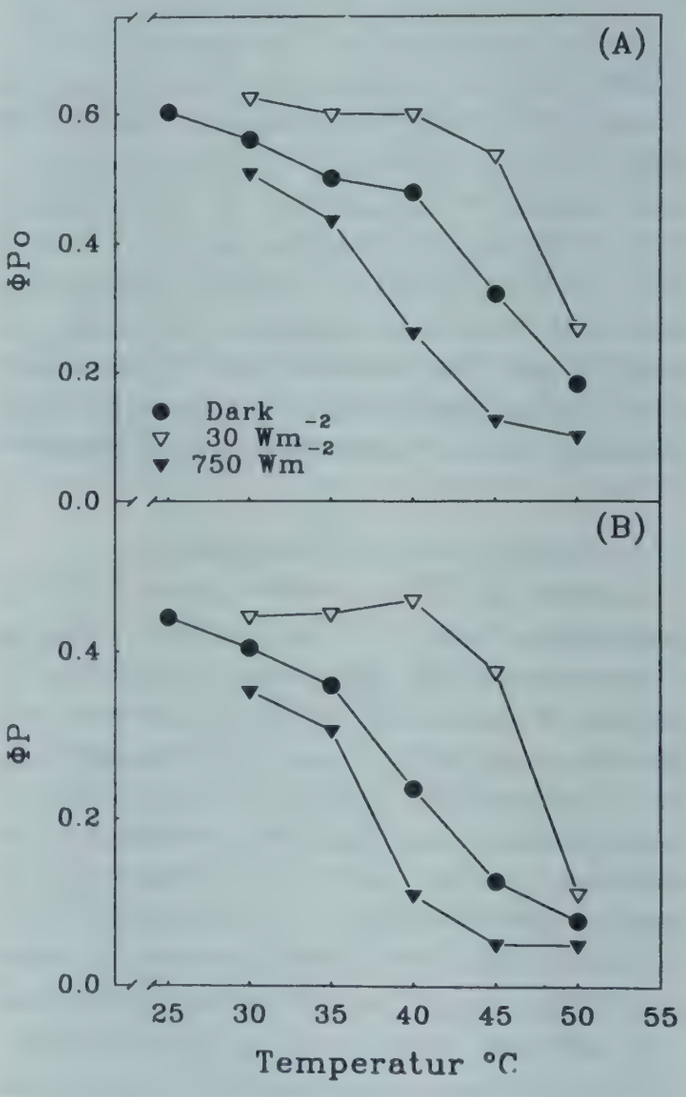

Fig. 4 — Synergistic and antagonistic effects of high (750 Wm^{-2}, closed triangles) and low light (30 Wm^{-2}, empty triangle) respectively on heat damage in pea leaves on ϕ *Po (A) and* ϕP (B). Leaves were exposed to different conditions for 30 min and dark adapted for 20 min before the measurements. The modulated Chl *a* fluorescence measurements were performed at room temperature by irradiating them with 100 Wm^{-2} blue actinic light. Other experimental details were the same as in Fig. 1 (Srivastava and Strasser[79] with permission)

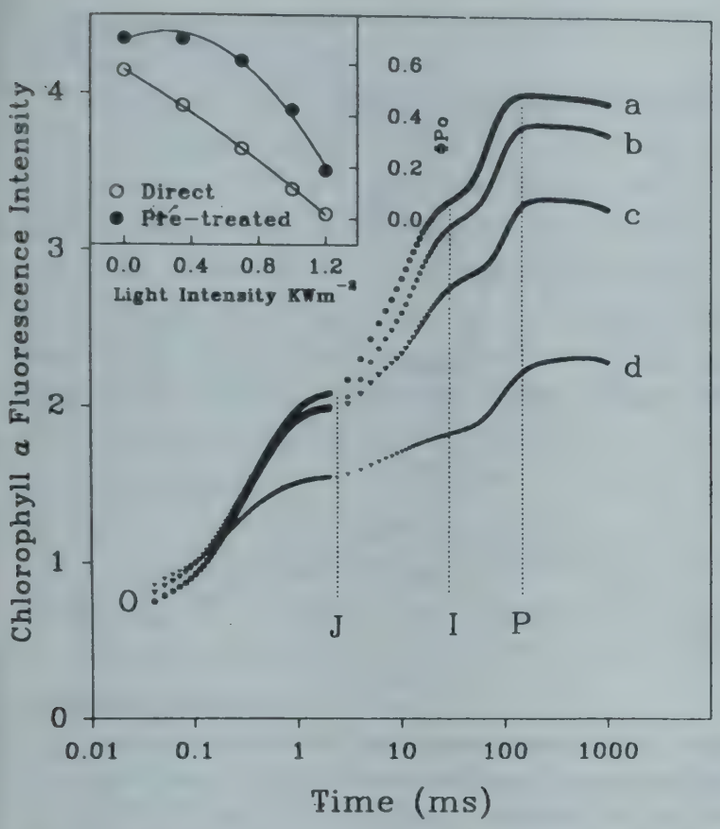

Fig 5 — Effect of pretreatment (30 Wm^{-2} at 30°C for 30 min) on the changes in the Chl *a* fluorescence induction curve [measured with PEA, Hansatech, For detail see Strasser *et al.*[80]]. Representative curves are: (a) dark adapted control sample; (b) 30 min of pretreatment at 30°C with 30 Wm^{-2}; (c) pretreated sample exposed to 750 Wm^{-2} at 35°C for 30 min and (d) directly exposed to 750 Wm^{-2} at 35°C for 30 min. The insert shows the maximum quantum efficiency (ϕPo) of pea leaves after exposing them to different light intensities at 35°C for 30 min. After the treatment, leaves were dark adapted for 20 min and modulated Chl *a* fluorescence measurements were performed at room temperature as described in Fig. 1. Leaves were either exposed directly (empty circles) or after pretreatment at 30°C and 30 Wm^{-2} blue light for 30 min (closed circles) (modified from Srivastava and Strasser[79], with permission).

exposed to 750 Wm^{-2} for 15 min after preheat and light treatment (30°C together with 30 Wm^{-2} for 30 min) (curve c) (for complete explanation of the O, J, I and P steps of the Chl *a* fluorescence induction curves[80]). Data obtained in the steady state conditions also show that maximum quantum efficiency (ϕ,*Po*) was much less affected in the leaves subjected to photoinhibition which were preheated to 30°C in comparison to the control leaves (Fig. 5). From these results one can draw the conclusion that a moderate and brief elevation of leaf temperature markedly stabilizes PSII against photoinhibition. The exact mechanism of heat induced photoprotection of PSII is not known. However, temperature is known to exert a strong influence on the physical properties of the lipid composition[81,82]. Considering the role played by lipid protein interaction in the maintenance of photosystem[83], one can speculate that preheat adaptation changes the conformation of PSII which somehow results in photoprotection of PSII reaction centers against strong light. Stapel *et al.*[84] observed higher resistance of barley against photoinhibition after heat treatment and they have correlated the results with the accumulation of heat shock protein (HSP 26) which protect the plants from photoinhibition.

3.4 Water Stress and Photoinhibition

Large quantity of water are absorbed by land plants. Most of it flows through the plants and is lost by transpiration, which occurs most rapidly when stomata are open for photosynthesis. Water stress has both stomatal (restricted CO_2 availability) and non-stomatal (direct inhibition of photosynthesis) components. As water stress increases during drought, photosynthesis and stomatal conductances decrease as a result of water deficit both in the roots[85] and in the shoots[86]. The reduced photosynthetic capacity decreases the ability of chlorophyllous cells to utilize the absorbed light quanta, and the reduced stomatal conductances lower the ability of leaves to dissipate the absorbed energy as latent heat. Water stress has been shown to predispose leaves of plants to photoinhibition[87-89]. Investigation of the interaction between full sunlight and water stress was made by Björkman and Powles[88] with the sun plant *Nerium oleander* grown under full sunlight or at only 3% sunlight. With the development of severe water stress (-5 MPa), electron transport of both PSII and PSI and the variable chlorophyll fluorescence was inhibited in leaves of plants kept in full sunlight or 3% sunlight. However, the onset was earliest and the severity of photoinhibition was greatest in plants maintained under full sunlight during the period of water stress. In another study, Downton[90-91] analyzed measurements of variable fluorescence in grape leaves and observed larger effects at low water when dehydration developed under high light than under low light. ögren and öquist[91] measured the gas exchange of leaves of *Salix* acclimated to a low light environment and found that photoinhibition was enhanced by low water. Figure 6 shows a typical water stress effect on photoinhibitory damage measured as maximum

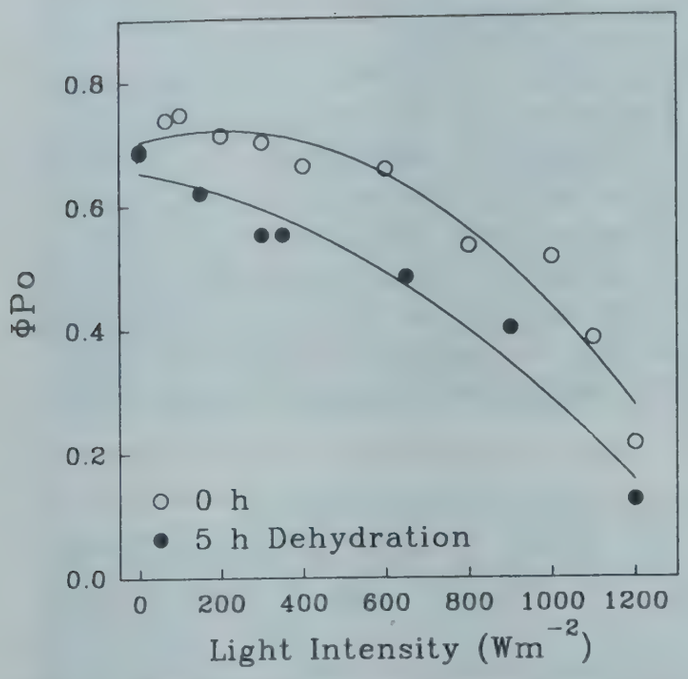

Fig. 6 — Effect of 20 min exposure to various fluence rates of white light on the maximal photochemical efficiency of PSII (ϕPo) of pea leaves dehydrated for 0 or 5 h. After the treatment, leaves were dark adapted for 20 min at room temperature and $F_s^{\,1}$, $F_o^{\,1}$ and $F_m^{\,1}$ were measured in steady state as described in Fig. 1 Srivastava and Strasser, (unpublished results).

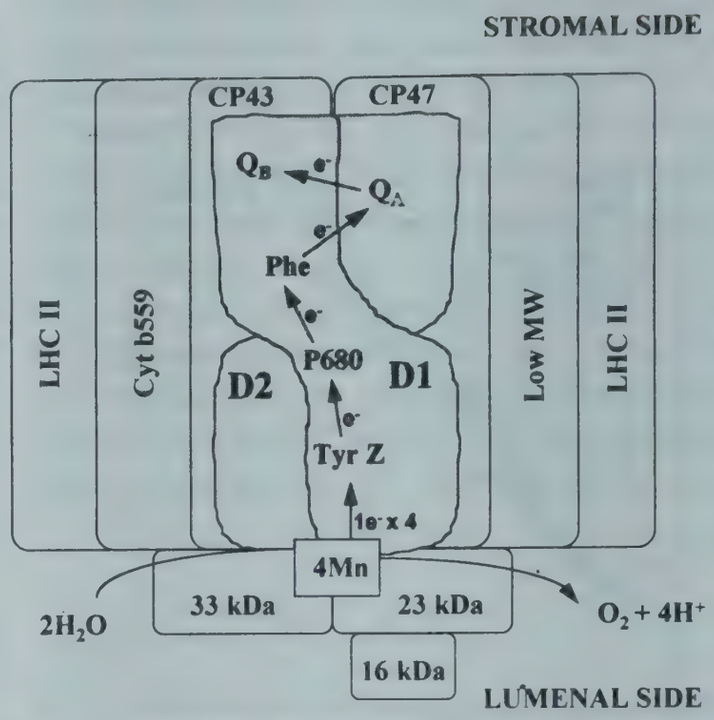

Fig. 7 — A schematic presentation of PS II in higher plants. The central part of the figure shows the D1, D2 protein heterodimer with bound redox components. The arrows indicate the electron transfer pathway from water to the secondary quinone acceptor Q_B. LHC: light harvesting complex, Low MW: low molecular weight proteins, CP: chlorophyll proteins

quantum efficiency (ϕ,*Po*) of pea leaves in steady state condition. It also demonstrates that 5 h of dehydration predisposes the photodamage significantly.

4 Biochemical Basis of Photoinhibition

Light induced damage is targeted mainly to PS II and leads to inactivation of electron transport and subsequent oxidative damage of the reaction center. Some mechanisms known so far regarding the damage to the photosynthetic apparatus evident with Photoinhibiton are described here.

4.1 Photosystem II

There is an evidence which shows that light- induced damage is targeted mainly to PSII and leads to inactivation of electron transport and subsequent oxidative damage of the reaction center in particular of the D1 protein[16]. According to the present knowledge, electron transport in PSII centers is initiated by charge separation between the pigment P680 in the first excited singlet state (P*680) and pheophytin, and ultimately results in the transfer of an electron from the secondary donor (Z, a tyrosine residue on the D1 protein) to the primary and secondary quinone-type acceptor Q_A and Q_{92} (see model in Fig. 7 for more detail). The chlorophyll *a* fluorescence yield of a single PSII unit rises from a low to a high value as Q_A is reduced to Q_{A^-}. Photoinhibited thylakoids show an impaired electron transport from P680 to Q_A. Electron transport through PSII is inhibited when photoinhibition is induced by an excessive PFD. The inhibition of PSII electron transport, during photoinhibition has been correlated with the loss of PSII Chl *a* fluorescence yield. Numerous determinations at room-temperature fluorescence show the loss of fluorescence yield during Photoinhibition. From the light induced absorption changes of pheophytin, Demeter *et al.*[93] concluded that photoinhibitory light treatment primarily causes an inhibition of charge separation between P680 and pheophytin. Using electron paramagnetic resonance spectroscopy, Styring *et al.*[94] indicated that photoinhibition inhibits the electron transfer between pheophytin and Q_A probably by impairment of the function of Q_A. At a given light flux density, the susceptibility of PSII to photoinhibition depends on the absorption cross section. Therefore, genetically shade-adapted plants,

having a larger antennae size than sun plants, exhibit stronger photoinhibition[18,35].

The analysis of the biphasic rate of growth of the area over the Chl *a* fluorescence induction curve in the presence of DCMU reflects the function of two distinct populations of PSII centers, termed PS IIα and PS IIβ, respectively[95]. The rates of Q_A^- formation by PS IIa and PS IIb are about 2-3 times faster than those of PS IIb. These two components reflect different rates of light absorption which could be caused by different absorption cross-sections of the light harvesting pigments in PS IIa and PS IIβ centers. PS IIα has an absorption cross-section of about 2-3 times larger than that of IIβ. Furthermore, it was shown that PS II centers are more susceptible to excess light than the PS IIα centers95 probably because of larger antenna size of PS IIα [95-98].

Cleveland and Melis[99] observed an enhanced photoinhibition of thylakoid after pretreatment with hydroxylamine, which inactivates the water-oxidation system and inhibits electron donation to P680 and thereby increases the lifetime of the oxidized P680. The latter is known to be a quencher of Chl *a* fluorescence[100]. This trapped $P680^+$ may lead to other destructive molecular changes. The probability of such events increase either by high excitation density in the antennae or alternatively by prolonged lifetime of $P680^+$, as in the case of limiting electron donation. Callahan *et al.*[101] and Wang *et al.*[102] also showed increased susceptibility of PSII after inactivation of water splitting enzyme. Curwiel and van Rensen[103] have reported proton leakiness of the thylakoid membranes after photoinhibition treatment.

On the other hand, a well known molecular change related to PSII photoinhibition is an inactivation and degradation of the 32 kDa Q_B-binding protein[16,20,22]. Many studies suggest that 32 kDa protein or specifically Q_B binding site is the initial site of photoinhibition. Excess light is supposed to induce structural changes of the protein that renders it inactive for electron transfer reactions.

Although most of the changes induced by photoinhibition are located on 32 and 34 kDa proteins[22], high light may also cause alteration of other proteins. It has been suggested that a 9 kDa phosphoprotein is involved in photoinhibition of PSII particles[104]. In the chilling sensitive plant *Zea mays*, photoinhibition treatments at chilling temperatures cause accumulation of a chlorophyll-binding 31 kDa protein in the thylakoids[105]. This effect was correlated with a decrease in the efficiency of excitation energy transfer from the light-harvesting complex to PSII. Photoinhibition also results in rapid oxidation of cytochrome b-559 and a change of cytochrome b-559 from its high potential form to its low potential form. The potential shift of cytochrome b-559 by photoinhibition induces early conformational changes in PSII[106]. They believe that this change reveals an electron transfer pathway in PSII that functions to protect the reaction center against excess light energy.

In spite of the above results, the problem of primary sites of photoinhibition is still not solved but readers are referred to several molecular models leading to PSII inactivation[107].

4.2 Photosystem I

Electron transport through PSI can be inhibited by exposure of the photosynthetic apparatus to excess visible light. The degree of photoinhibition of PSI can be equal to[11] or less than[43,108-110] that of PSII, or in some cases negligible. The site of photoinhibition is at[109] or very close to the PSI reaction centers[13]. For the inhibition of the electron transport capacity of PSI, the presence of O_2 is essential[12,111,112]. Terashima *et al.*[113] measured the quantum yield of photosynthetic electron flow through PSI and PSII of thylakoid membranes of chilled leaves of *Cucumis sativus* and concluded that at least in this plant the PSI is more susceptible to photoinhibition than PSII. Sonoike and Terashima[114] further suggested that photoinhibitory processes in the reaction center of PSI go through three steps, the inactivation of the acceptor side, the destruction of the reaction center chlorophyll and the degradation of reaction center sub-units.

4.3 Production of Active O_2

Chloroplasts of higher plants are capable of oxygen metabolism in two respects: besides catalyzing water oxidation, they possess the potential for generating several forms of destructive oxygen species[52,58]. Photoreduction of molecular oxygen, the Mehler[57] reaction, is an unavoidable process that produces superoxide anion radical (O_2^-). Dismutation of O_2^- results in the formation of hydrogen peroxide

(H_2O_2) and the reaction between O_2^- and H_2O_2 may create the highly reactive hydroxyl radicals (·OH). The toxicity of active oxygen lies in the fact that it can react with numerous cell components, thereby causing inactivation of enzymes, pigment bleaching, lipid peroxidation and protein degradation. Kyle[20] has suggested that impairment of D1 protein in the PSII reaction center may result from oxygen radical attack on the amino-acid residue of the peptide chain.

In addition to the active oxygen species mentioned above, photosynthetic organisms are continuously faced with the production of highly toxic singlet oxygen ($^1O_2$*). Absorption of light leads to formation of excited singlet chlorophyll (^{1}Chl*) that may be converted into triplet state (^{3}Chl*) by intersystem crossing. This allows a reaction with ground state oxygen ($^3O_2$) to occur resulting in toxic $^1O_2$* that has similar deleterious effects as ·OH[115,116]. In the recent past, a series of experiments have been done using paramagnetic resonance spectroscopy experiments with the singlet oxygen trap 2,2,6,6- tetramethylpiperidine[117,118]. The results show that under photoinhibitory conditions, singlet oxygen is present in thylakoids and photosystem II core complex preparations but could not be produced in photosystem I[117]. They have also shown that singlet oxygen did not produced under anaerobic conditions[118]. Using the same technique, Hideg *et al.*[119] could demonstrate that singlet oxygen was detected only in samples undergoing acceptor side induced photodamage. On another hand the donor side induced photodamage was dominated by hydroxyl radicals. By using the chemical trapping techniques for singlet oxygen formation, Telfer *et al.*[120] reached on the conclusion that singlet oxygen is formed with in the hydrophobic interior of the reaction center attacks the chlorophylls of P680 and also the amino acids.

Several scavenger systems minimize the damage in the normal condition when the plants are stressed by photoinhibition. When the scavenger system or repair process is insufficient, it leads to inactivation of enzymes, chlorosis, loss of integrity and cell death[52,59,65,121].

5 Photoprotection

Upon the absorption of more light than can be utilized through photosynthetic electron transport, several photoprotective mechanism can prevent the potentially damaging accumulation of excitation energy in the photochemical apparatus. Some of main photoprotective mechanism are discussed below.

5.1 Prevention of Excessive Light Absorption

Photosynthetic cells receiving an excessive PFD could reduce the potential for photoinhibition by physically reducing the total surface area of chloroplasts exposed to strong light. Such responses include the movement of chloroplasts[122] and whole leaves[123,124]. When the aquatic plant *Elodea* was irradiated with high PFD, all the chloroplasts aggregated at the cell wall, and over a certain range of PFD, they did not suffer any damage. However, after prolonged exposure to sunlight, the chloroplast movement did not prevent photoinhibition[122].

In the absence of stress, several species exhibit solar tracking to maximize light interception by the leaf surface[125]. These plants also possess the ability to minimize light interception when subjected to any environmental stress. Over longer durations, leaves may develop certain leaf angles that minimize light absorption when plants are growing in excessive light[126]. Leaves may develop greater surface reflectance pubescence, by formation of waxy cuticle or by accumulation of salt on the surface, under conditions when light is excessive[127].

5.2 Removal of Excess Excitation Energy Directly Within the Light Harvesting System and the Xanthophyll Cycle

Upon the absorption of more light than can be utilized through photosynthetic electron transport, several photoprotective mechanisms can prevent the potentially damaging accumulation of excitation energy in the photochemical apparatus. As long ago as 1978, Butler[100] had reviewed the alternatives of energy dissipation and distribution within the photosynthetic apparatus, including the potential for spillover of exciton energy to PSI and so called state 1 and state 2 transitions where state 1 is the state after excitation with light absorbed in PSI, and state 2 is the state after excitation with light absorbed in PSII. Studies with an intertidal alga *Porphyra* document that substantial spillover from PSII to PSI can occur,

and this spillover was suggested to contribute to the avoidance of photoinhibition in this organism[128].

The protective role of carotenoids in preventing photooxidative damage is well known[129]. Carotenoids prevent photooxidative damage in two ways:

1 By scavenging singlet O_2 ($^1O_2$*), which is formed via the reaction of triplet excited Chl (^{3}Chl*) with triplet O_2 ($^3O_2$):

$$^1\text{Chl} + h \rightarrow {}^1\text{Chl}^* \rightarrow {}^3\text{Chl}^* \xrightarrow{{}^3O_2} {}^1\text{Chl} + {}^1O_2^*$$

$$^1O_2^* + {}^1\text{Car} \xrightarrow{{}^3O_2} {}^3\text{Car}^* \rightarrow {}^1\text{Car} + \text{Heat}$$

2 By quenching ^{3}Chl* directly and so prevent singlet O_2 production:

$$^3\text{Chl}^* + {}^1\text{Car} \rightarrow {}^3\text{Car}^* + {}^1\text{Chl}$$

$$^3\text{Car}^* \rightarrow {}^1\text{Car} + \text{Heat}$$

By measuring the time resolved luminescence emission at 1270nm, Telfer *et al.*[130] have also confirmed that β-carotene can act as an effective quencher of singlet oxygen in the photosystem II reaction center.

Another way in which a quenching/deactivation of the singlet excited state of chlorophyll can occur is via energy transfer to zeaxanthin, followed by radiationless energy dissipation[5,15,27,28]. Zeaxanthin is a pigment of xanthophyll cycle situated in the supramolecular complexes of the thylakoid membrane.

The xanthophyll cycle consists of light dependent conversions of three xanthophylls in a cyclic reaction involving the de- epoxidation of diepoxide violaxanthin in to monoepoxide antheraxanthin to the epoxide free zeaxanthin, and an epoxidation sequence in the reverse direction[131-133]. The xanthophyll cycle is present in the thylakoid membranes of most of the green plants[5,131,132]. Under excess of light, zeaxanthin accumulates in leaves and in chloroplasts and the reconversion of zeaxanthin to violaxanthin occurs upon return to the non-excessive light. This process is controlled by several regulatory processes[131-133].

Several correlations have been shown between the increase in the level of zeaxanthin and increase in energy dissipation as estimated from chlorophyll fluorescence quenching[5,15] leading to the suggestion that zeaxanthin mediates the dissipation of absorbed excess energy as heat. Usually the photoprotective heat dissipation is measured as nonphotochemical quenching (NPQ) of the PSII chlorophyll *a* fluorescence. Evidence for a casual relationship between zeaxanthin and thermal energy dissipation has also been obtained by using DTT, an inhibitor of the de-epoxidation[134-137]. A linear relationship between the amount of zeaxanthin and NPQ has been observed when leaves are exposed to excess light. However, it has been shown that the violaxanthin-antheraxanthin-zeaxanthin cycle can be fully activated in such a way that the transformation of violaxanthin to zeaxanthin did not cause any change in fluorescence (and therefore in the dissipation) properties[138]. Therefore, zeaxanthin alone is not enough to trigger excitation energy dissipation.

In the recent past, several studies have shown the combined presence of zeaxanthin (antheraxanthin) and a low pH within the photosynthetic membrane and confirm that both low pH and the presence of zeaxanthin is obligatory for NPQ to occur[28,139,140]. For example, NPQ was induced in darkness by protonation of zeaxanthin-containing chloroplast membrane but not in zeaxanthin free chloroplasts[141]. In addition, when zeaxanthin was allowed to be reconverted into violaxanthin under excess light it led to a loss of energy dissipation activity in spite of the continued presence of low pH[142].

Several hypotheses have been presented about the nature of involvement of zeaxanthin in energy dissipation. Horton and co-workers[143,144] have proposed that zeaxanthin modifies the pH response of a thermal energy dissipation process to allow this process to occur at pH values presumably normally found *in vivo*. Neubauer and Yamamoto[145] furthermore suggested, that the effect of Mehler peroxidase reaction also occurs via increased formation/activation of zeaxanthin. Demmig-Adam[5,28] suggested the de-excitation of singlet excited state of chlorophyll (^{1}Chl*) by zeaxanthin/antheraxanthin in presence of low pH as shown in Eq.(1).

$$^1\text{Chl}^* + H^+ \xrightarrow[\text{internal conversion}]{\text{Zea or Anth}} \text{Chl} \qquad \ldots(1)$$

In alternative proposed mechanism[146] [as shown in Eq. (2)] H^+activates the singlet energy transfer to zeaxanthin followed by internal conversion to the ground state of zeaxanthin releasing the energy as heat:

native proposed mechanism[146] [as shown in Eq. (2)] H^+ activates the singlet energy transfer to zeaxanthin followed by internal conversion to the ground state of zeaxanthin releasing the energy as heat:

$$^1Chl^* + Zea \text{ or } Anth \xrightarrow[\text{singlet energy transfer}]{H^+} Chl + {}^1Zea^* \text{ or } {}^1Anth^* \quad ...(2)$$

In recent studies, Gilmore *et al.*[147] have observed that in chloroplasts where photochemistry was blocked by diuron, the increase in the fraction of short life (400 ps) time chlorophyll fluorescence component was accompanied by a parallel decrease in the fraction of lifetime of a longer lifetime (2 ns) of fluorescence component, and they interpreted their data in terms of the formation of a complex that has a low quantum yield of fluorescence and thus increased rate constant of the heat loss within it. These lifetime of fluorescence (τ) studies are the only ones that prove that the observed changes are changes in quantum yield of fluorescence (ϕ) and thus in rate constant of heat dissipation since $\tau = \phi^* \tau_o$ where τ_o is intrinsic life time of fluorescence, and $\phi = k_f/\Sigma ks$. By using the same technique of life time of fluorescence measurements, recent studies by Gilmore *et al.*[148,149] have led to the conclusion that combined effect of xanthophyll cycle and Δ pH cause major conformational changes in the pigment-protein complexes of the PSII inner or core antennae that switch a normal PSII unit to an increased rate constant of heat dissipation. Detailed discussion on the physical mechanism of the energy dissipation via xanthophylls are described elsewhere[28,29].

Other suggested dissipative mechanisms, within the photochemical apparatus include a charge-recombination process within the reaction centers[150-152] as well as dissipative electron cycle around the reaction center of PSII[23,151,152].

5.3 Removal of Active O_2 Formed in the Photochemical Apparatus

As discussed above, two main forms of active oxygen are involved for photooxidative damage, the superoxide radicals, O_2 and singlet oxygen, $1O_2$. In the Mehler reaction, O2 acts as an electron acceptor for PS I[58]. Photoreduction of O_2 increases when the supply of CO_2 is limited or the Calvin cycle is inhibited. Mechanisms for the removal of these potentially destructive species have been elucidated over the past few years and thoroughly considered in many reviews[52,58,59,65,66] which have appeared earlier. The superoxide anion radical, O_2^- is dismutated to hydrogen peroxide and oxygen by superoxide dismutase, located in the stroma and lumen of the chloroplasts

$$O_2^- + O_2^- + 2H+ = H_2O_2 + O_2$$

The enzyme superoxide dismutase has been shown to prevent photooxidative damage in plant tissues[153-155].

Ascorbate peroxidase then catalyzes the reduction of the toxic peroxide to water and producing ascorbate radicals, monodehydroascorbate (MDA). The MDA rereduced directly by NADPH (via monodehydroascorbate reductase) and secondly, to dehydroascorbate, which is re-reduced (via dehydroascorbate reductase) by reduced glutathione which is in turn was also reduced by NADPH (via glutathione reductase)[52,59].

2 ascorbate $+H_2O_2$ =2 MDA

2 MDA +NADPH =2 ascorbate +NAD(P)

MDA +MDA =dehydroascorbate +ascorbate

Various components of this ascorbate metabolism have been found in increased amounts under excess light in leaves acclimated to such conditions, particularly at chilling temperatures[121,156,157]. Chloroplasts of leaves, developed under intense light environment, posses greater quantities of different components of the ascorbate metabolism cycle than the leaves developed under shade[156]. Ascorbate is also needed for the xanthophyll cycle. So, in addition to the support for the linear electron flow via its consumption of NADPH and H_2O_2, ascorbate facilitates the formation of zeaxanthin, and according to a recent theory, zeaxanthin is involved in the thermal energy dissipation (see section 5.2). It has been hypothesized that the Mehler peroxidase reaction induces the development of a large transthylakoid pH gradient and in turn promotes significant zeaxanthin formation[145].

Hydrogen peroxide can also be removed by catalase[158]. A flavonol (kaempferol) also decreases the photooxidative damage in chloroplasts[159,160].

Another species which is highly reactive, that can be formed in the thylakoid membrane, is the $^1O_2$ through interaction with the excited triplet state of chlorophyll. As discussed earlier, the carotenoid pig-

ments in the thylakoid membrane have a protective function by interacting with triplet state chlorophyll and quenching $^1O_2$. They dissipate the excited energy as heat. A series of experiments support the role of cytochrome b 559 in oxidizing anion radicals (for more detail see ref.[161]). Whether any of these reactions protect PSII against photodamage remains to be proven.

5.4 Inactivation/Turnover of PS II

The D1 protein of the PS II carries several of the primary components of the photochemical reaction sequence that are affected during the inactivation of PSII through exposure to high PFD[98,101,162]. Light also stimulates the D1 protein turnover. This turnover consists of the assembly of complexes, which take place within the stromal lamellae, followed by migration of these complexes into the granal lemellae and a degradation process involving the translocation of PSII components from granal to stromal lamellae[163-165]. There have been many reports that D1 protein gets damaged by high light exposure and subsequently replaced[16,20]. In several studies, investigators have used protein inhibitors and found that recovery from photoinhibition can be dependent on the protein synthesis[74,75,166,167]. It was therefore suggested that the migration of PS II complex carrying D1 between stromal and granal thylakoids represents a PS II repair cycle involving migration of damaged PS II centers out of granal thylakoids and migration of undamaged PS II centers into the stromal lamellae. A model has been proposed suggesting that the extent of photoinhibition is determined by the relative rate of damage and repair during exposure to excessive light in leaves[16].

Concluding Remarks

Plants in their natural environment are well-adapted to minimize photoinhibitory damage which only occurs under very extreme conditions or upon the imposition of an unusual combination of stresses. The factors causing modifications in plants that leads to natural resistance and the mechanisms which mediate enhanced response of the system to photoinhibition are not fully understood. Photoinhibition stress should not be viewed in isolation. Rather, it should be viewed within the perspective of the overall cellular response to stress. The interaction between different stress factors suggests that the photoinhibitory stress on the plants monitored under controlled environmental conditions in the laboratory, where the effects of a defined stress are studied in a "one-factor-one-response" test, might be quite different from the plant's response in the field, where several factors usually change simultaneously and interact. The photoprotection and heat protection by training the plants with pre-mild heat treatment and heat protection by low light suggest that the present terrestrial plants are well tuned for their natural environment for every combination of changes in the present daily cycle of the earth. The interaction of different mechanisms are complex and provide flexibility for regulation. Extreme environmental conditions or drastic manipulations may compromise the plants ability to acclimate. Changes in the global environment, such as increased environmental CO_2 and temperature fluctuations, which are a product of human activities may drive regulatory mechanism to instability.

Infinite specific cases can be cited concerning the interaction of light as stressor on plants. But the question arises how stress can be seen in a conceptual way which allows a physical description and therefore a quantification. All cases reported here can be seen in a highly simplified stress concept given by Larcher[168] that "every organism experiences stress, although the way in which it is expressed differs according to its level of organization. After sensing a certain stress, plants lead to an initial destabilization of functions, followed by improved resistance. But if the limits of tolerance exceed, a permanent damage or even death may result. Thus, stress contains both constructive and destructive elements. It is the selection factor and the driving force which improve the resistance of the organism and thus the evolution". This concept has been linked to thermodynamics by Strasser[169] in such a way that the driving force for state changes has been defined as suboptimality of the biological state in a given environment. Further work will show how changes of the environmental conditions can modify the photosynthetic machinery to extend its buffer capacity against photoinhibition to allow an optimum behavior, optimum growth with an optimal vitality

References

1 Caldwell M M, in Encyclopedia of Plant Physiology, edited by O L Lange, P S Nobel, C B Osmond and H Ziegler (Berlin: Springer) **Vol. 12a**: *Physiol Plant Ecol*, **I**, (1981) pp 170-197.

2 Ensminger P A, *Physiol Plant*, **88** (1993) 501-508.

3 Powles S B, *Annu Rev Plant Physiol*, **35** (1984) 15-44.

4 Baker N R & Horton P, in *Photoinhibition*, edited by D J Kyle, C.B. Osmond and C J Arntzen (Elsevier Science Publisher) 1987, pp 145-168.

5 Demmig-Adams B & Adams W W III, *Annu Rev Plant Physiol Plant Mol Biol*, **43** (1992) 599-626.

6 Björkman O & Holmgren P, *Physiol Plant*, **16** (1963) 889-914.

7 Powles S B & Osmond C B, *Aust J Plant Physiol*, **5** (1978) 619- 629.

8 Forti G & Jagendorf A T, *Biochim Biophys Acta*, **44**(1960) 34-40.

9 Avron M, *Biochim Biophys Acta*, **44** (1960) 41-48.

10 Jones L W & Kok B, *Plant Physiol*, **41** (1966) 1037-1043.

11 Satoh K, *Plant Cell Physiol*, **11** (1970) 15-27.

12 Satoh K, *Plant Cell Physiol*, **11** (1970) 29-38.

13 Satoh K, *Plant Cell Physiol*, **11** (1970) 187-197.

14 Björkman O, Boardman N R, Anderson J M, Thorne S W, Goodchild D J & Pyliotis N A, *Carnegie Inst Washington Yearb*, **71** (1972) 115-135.

15 Demmig-Adam B, *Biochim Biophys Acta*, **1020** (1990) 1-24.

16 Aro E M, Virgin I & Andersson B, *Biochim Biophys Acta*, **1143** (1993) 113-134.

17 Long S P, Humphries S & Falkowski P G, *Annu Rev Plant Physiol Plant Mol Biol*, **45** (1994) 633-62.

18 Björkman O, in Encyclopedia of plant Physiology, edited by O L Lange, P S Nobel, C B Osmond and H Ziegler (Berlin, Springer) *Physiol Plant Ecol* **I**, (Vol. 12a, 1981) pp 57-107.

19 Critchley C, Aust *J Plant Physiol*, **15** (1988) 27-41.

20 Kyle D J, in *Photoinhibition*, edited by D J Kyle, C B Osmond and C J Arntzen (Elsevier Science Publisher) 1987, pp 197- 226.

21 Ohad I, Adir N, Koike H, Kyle D J & Inoue Y, *J Biol Chem*, **265** (1990) 1972-1979.

22 Krause G H, *Physiol Plant*, **74** (1988) 566-574.

23 Baker N R, *Physiol Plant*, **81** (1991) 563-570.

24 Young A J & Britton G, in *Stress Responses in Plants: Adaptation and Acclimation Mechanism*, edited by R G Alsher and J R Cumming (Wiley-Liss Inc) 1990, pp 87-112.

25 *Photoinhibition of Photosynthesis: Molecular Mechanism to the Field*, edited by N R Bakar & J R Bowyer (Bios Scientific Publisher. Oxford, UK), 1994.

26 Chow W S, *Adv Mol Cell Biol*, **10** (1994) 151-196.

27 Demmig-Adams B & Adams WW, *Trends Plant Sci*, **1** (1996) 21-26.

28 Demmig-Adams B, Gilmore A M & Adams W W, *FASEB J*, **10** (1996) 403-412.

29 Gilmore A M, *Physiol Plant*, (in press).

30 Neale P J, (see ref. 4) 1987, pp 39-65.

31 Falkowski P G, Green R & Kolber Z, (see ref. 25) 1994, pp 407-432.

32 Ting C S & Owens T G, *Plant Physiol*, **106** (1994) 763-770.

33 Bose S, Herbert S K & Fork D C, *Plant Physiol*, **86** (1988) 946-950.

34 Osmond C B, Ramus J, Levavasseur G, Franklin L A & Henley W J, *Planta*, **190** (1993) 97-106.

35 Anderson J M & Osmond C B, (see ref. 4) 1987, pp 1-38.

36 Gauhl E, *Oecologia*, **22** (1976) 275-286.

37 Powles S B & Thorne S W, *Planta*, **152** (1981) 471-477.

38 Oberhuber W & Bauer H, *Planta*, **185** (1991) 545-553.

39 Björkman O & Schäfer C, *Phil Trans R Soc Lond*, **B 323** (1989) 309-311.

40 öquist G, Anderson J M, McCaffery S & Chow W S, *Planta*, **188** (1992) 422-431.

41 Osmond C B, (see ref. 25) 1994, pp 1-24.

42 Osmond C B, (see ref. 4) 1987, pp 1-38.

43 Krause G H and Cornic G, (see ref. 4), 1987, pp 169-196.

44 Gong H, Nilsen S & Allen J F, *Biochim Biophys Acta*, **1142** (1993) 115-122.

45 Sundby C, *FEBS Lett*, **274** (1990) 77-81.

46 Eloff J N, Steinitz Y & Shilo M, *Appl Environ Microbiol*, **31** (1976) 119-126.

47 Kaplan A, *J Exp Bot*, **32** (1981) 669-677.

48 Asami S and Akazawa T, *Plant Physiol*, **62** (1978) 981-986.

49 Cornic G, *C.R. Acad Sci Paris*, **282** (1976) 1955-1958.

50 Tolbert N E, *Annu Rev Plant Physiol*, **22** (1971) 45-74.

51 Krause H G, Koster S & Wong S C, *Planta*, **165** (1985) 430-438.

52 Asada K, and Takahashi M, (see ref. 4) 1987 pp 227-287.

53 Richter M, Ruhle W & Wild A, *Photosynth Res*, **24** (1990) 237- 243.

54 Godde D, Buchhold J, Ebbert V & Oettmeier W, *Biochim Biophys Acta*, **1140** (1992) 69-77.

55 Powles S B, Chapman K S R & Whatley F R, *Plant Physiol*, **69** (1982) 371-374.

56 Boyle F A & Keys A J, *Photosynth Res*, **3** (1982) 105-111.

57 Mehler A H, *Arch Biochim Biophys*, **33** (1951) 65-77.

58 Asada K, (see ref. 25), 1994, pp 129-142.

59 Foyer C H, Lelandais M & Kunert K J, *Physiol Plant*, **92** (1994) 696-717.

60a Havaux M and Davaud A, *Photosynth Res*, **40** (1994) 75-92.

60b öquist G, Green D H and ögren E, (see ref. 4) 1987 pp 67-87.

61 Neuner G & Larcher W, *Photosynthetica*, **25** (1991) 257-266.

62 Hetherington S E, He J & Smillie R M, *Plant Physiol*, **90** (1989) 1609-1615.

63 Baker N R, East T M & Long S P, *J Exp Bot*, **34** (1983) 189-97.

64 Weis E, *Plant Physiol*, **70** (1982) 1530-1534.

65 Halliwell B, in *Superoxide Dismutase*, edited by L W Oberley (Florida, CRC Press) **Vol 1**, 1982, pp 89-123..

66 Elstner E F, *Ann Rev Plant Physiol*, **33** (1982) 73-96.

67 Huner N P A, öquist G, Hurry V M, Krol M, Falk S, & Griffith M, *Photsynth Res*, **37** (1993) 19-39.

68 Briantais J M, Ducruet J M, Hodges M & Krause G H, *Photosynth Res*, **31** (1992) 1-10.

69 Krause G H, (see ref. 25) 1994, pp 331-348.

70 Krause G H & Somersalo S, *Phil Trans R Soc Lond*, **B 323** (1989) 281-293.

71 Gillies S L & Vidaver W, *Physiol Plant*, **80** (1990) 148-153.

72 Gombos Z, Wada H & Murata N, *Proc Natl Acad Sci USA*, **91** (1994) 8787-8791.

73 Wise R R & Naylor A W, *Plant Physiol*, **83** (1987) 278-282.

74 Greer D H, Berry J A & Björkman O, *Planta*, **168** (1986) 253-260.

75 Greer D H, Ottander C & öquist G, *Physiol Plant*, **81** (1991) 203-210.

76 Srivastava A & Strasser R J, *Archs. Sci. Genève*, **48** (1995) 135-146.

77 Havaux M & Strasser R J, *Z Naturforsch*, **45c** (1990) 1133-1141.

78 Havaux M, Greppin H and Strasser R J, *Planta*, **186** (1991) 88- 98.

79 Srivastava A & Strasser R J, *J Plant Physiol*, **148** (1996) 445-455.

80 Strasser R J, Govindjee & Srivastava A, *Photochem Photobiol*, **61** (1995) 32-42.

81 Vander Meer B W, in *Biomembranes: Physical Aspects* edited by M Shinitzky (VCH, Weinheim, Germany) 1993, pp. 97-158.

82 Vigh L, Los D A, Horvath I & Murata N, *Proc Natl Acad Sci* USA, **90** (1993) 9090-9094.

83 Webb M S & Green B R, *Biochim Biophys Acta*, **1060** (1991) 133- 158.

84 Stapel D E, Kruse D E & Kloppstech K, *J Photochem Photobiol*, **21** (1993) 211-218.

85 Blackman P G & Davies W J, *J Exp Bot*, **36** (1985) 39-48.

86 Cornic G, (see ref. 25), 1994, pp 297-313

87 Ludlow M M, (see Ref. 4) 1987, pp 89-109.

88 Björkman O & Powles S B, *Planta*, **161** (1984) 490-504.

89 Havaux M, *Plant Cell Physiol*, **35** (1994) 757-766.

90 Downton W J S, *Plant Sci Lett*, **30** (1983) 137-143.

91 Ögren E & Öquist G, *Planta*, **166** (1985) 380-388.

92 Diner, B C & Babcock G T, in *Oxygenic Photosynthesis: The Light Reaction*, edited by D R Ort and C F Yocum, (Kluwer Academic Publisher), 1996, 213-247

93 Demeter S, Neal P J & Melis A, *FEBS Lett*, **214** (1987) 370- 374.

94 Styring S, Virgin I, Ehrenberg A and Andersson B, *Biochim Biophys Acta*, **1015** (1990) 269-278.

95 Neal P J & Melis A, *Biochim Biophys Acta*, **1056** (1991) 195- 203.

96 Govindjee, *Photosynth Res*, **25** (1990) 151-160.

97 Melis A, *Biochim Biophys Acta*, **1058** (1991) 87-107.

98 Lavergne J & Briantais J-M, in *Oxygenic Photosynthesis: The Light Reaction*, edited by D R Ort and C F Yocum (Kluwer Academic Publisher), 1996, 265-287

99 Cleland R E & Melis A, *Plant Cell Environ*, **10** (1987) 747- 752.

100 Butler W L, *Ann Rev Plant Physiol*, **29** (1978) 345-78.

101 Callahan F F, Becker D W & Cheniae G M, *Plant Physiol*, **82** (1986) 261-269.

102 Wang W Q, Chapman D J & Barber J, *Plant Physiol*, **99** (1992) 16-20.

103 Curwiel V B & van Rensen J S, *Physiol Plant*, **89** (1993) 97- 102.

104 Kuhn M, Thiel A & Böger P, *Z Naturforsch.*, **43c** (1988) 413-417.

105 Hyden D B, Baker N R, Percival M P & Beckwith P B, *Biochim Biophys Acta*, **851** (1986) 86-93.

106 Nedbal L, Samson G & Whitmarsh J, *Proc Natl Acad Sci* USA, **89** (1992) 7929-7933.

107 Ohad I, Keren N, Zer H, Gong H, Mor T H, Gal A, Tal S & Domovich Y, (see ref. 25) 1994, pp 161-177.

108 Satoh K & Fork D C, *Plant Physiol*, **70** (1982) 1004-1008.

109 Satoh K & Fork D C, *Photochem Photobiophys*, **4** (1982) 153- 162.

110 Cornic G, *Plant Physiol*, **78** (1985) 724-729.

111 Harvey G W & Bishop N I, *Plant Physiol*, **62** (1978) 330-336.

112 Powles S B & Björkman O, *Planta*, **156** (1983) 97-107.

113 Terashima I, Funayama S & Sonoike K, *Planta*, **193** (1994) 300- 306.

114 Sonoike K & Terashima I, *Planta*, **194** (1994) 287-293.

115 Mathis P & Schenck C C, in *Carotenoid Chemistry and Biochemistry*, edited by G. Britton and T W Goodwin (Pergaman Press, Oxford) 1981, pp 339-351.

116 Knox J P & Dodge A D, *Biochemistry*, **24** (1984) 889-896.

117 Hideg E & Vass I, *Photochem Photobiol*, **62** (1995) 949-952.

118 Hideg E, Spetea C & Vass I, *Photosynth Res*, **39** (1994) 191- 199.

119 Hideg E, Spetea C & Vass I, *Biochim Biophys Acta*, **1186** (1994) 143-152.

120 Telfer A, Bishop S M, Phillips D & Barber J, *J Biol Chem*, **269** (1994) 13244-13253.

121 Schöner S & Krause G H, *Planta*, **180** (1990) 383-389.

122 Drew E A, *Aquat Bot*, **7** (1979) 139-150.

123 Koller D, *Photochem Photobiol*, **44** (1986) 819-826.

124 Kao W Y & Forseth I N, *Environ Exp Bot*, **32** (1992) 153-161.

125 Ehleringer J R & Forseth I, *Science*, **210** (1980) 1094-1098.

126 Ehleringer J R, *Am J Bot*, **75** (1988) 680-689.

127 Mooney H A, Ehleringer J & Björkman O, *Oecologia*, **29** (1977) 301-310.

128 öquist G & Fork D C, *Physiol Plant*, **56** (1982) 56-62.

129 Cogdell R, in *Plant Pigments*, edited by T W Goodwin (T J Press Ltd., Padstaw, Cornwall, U K) pp 183-230.

130 Telfer A, Dhami S, Bishop S M, Phillips D & Barber J, *Biochemistry*, **33** (1994) 14469-14474.

131 Hager A, in *Pigments in Plants*, edited by F C Czygan (Fischer, Stuttgart) 1980, pp 57-79.

132 Siefermann-Harms D, in *Lipids and Lipid Polymers in Higher Plants*, edited by M Tevini and H K Lichtenthaler (Springer, Berlin) 1977, pp 218-230.

133 Yamamoto H Y, *Pure Appl Chem*, **51** (1979) 639-648.

134 Bilger W & Björkman O, *Photosynth Res*, **25** (1990) 173-185.

135 Demmig-Adam B, Adams III W W, Winter K, Meyer A, Schreiber U, Rereira J S, Krüger A, Czygan F & Lang O L, *Planta*, **177** (1989) 377-387.

136 Gilmore A M & Yamamoto H Y, *Plant Physiol*, **96** (1991) 635- 643.

137 Winter K & Königer M, *Planta*, **180** (1989) 24-31.

138 Meck E & Strasser R J, in *Progress in Photosynthesis Research*, edited by J Biggins (Martinus Nijhoff, Dordrecht) 1987, pp 709-712.

139 Pfündel E & Bilger W, *Photosynth Res*, **42** (1994) 89-109.

140 Gilmore A M & Yamamoto H Y, In *Photosynthetic Responses to the Environment*, edited by HY Yamamoto and C M Smith (American Society of Plant Physiologist) 1993, pp 162-165.

141 Gilmore A M & Yamamoto H Y, *Proc Natl Acad Sci, USA*, **89** (1992) 1899-1903.

142 Gilmore A M, Mohanty N & Yamamoto H Y, *FEBES Lett*, **350** (1994) 217-274.

143 Rees D & Horton P, *Biochim Biophys Acta*, **1016** (1990) 219- 227.

144 Noctor G, Rees D, Young A & Horton P, *Biochim Biophys Acta* **1057** (1991) 320-330.

145 Neubauer C & Yamamoto H Y, *Plant Physiol*, **99** (1992) 1354- 1361.

146 Frank H A, Cua A, Chynwat V, Young A, Goszlola D & Wasielewski M R, *Photosynth Res.*, **41** (1994) 389-395.

147 Gilmore A M, Hazlett T L & Govindjee, *Proc Natl Acad Sci, USA*, **92** (1995) 2273-2277.

148 Gilmore A M, Hazlett T L, Debrunner P G & Govindjee, *Photosynth Res*, **48** (1996) 171-187.

149 Gilmore A M, Hazlett T L, Debrunner P G & Govindjee, *Photochem Photobiol*, **64** (1996) 552-563.

150 Weis E & Berry J A, *Biochem Biophys Acta*, **894** (1987) 198- 208.

151 Rees D, Noctor G & Horton P, *Photosynthesis Res*, **25** (1990) 199-211.

152 Horton P & Ruban A, (see ref. 25) 1994, pp 111-128.

153 Tanaka K & Sugahara K, *Plant Cell Physiol*, **21** (1980) 601- 611.

154 Srivastava A & Tel-Or E, *J Environ Sci Health*, **A27** (1992) 261-272.

155 Mishra N P, Mishra R K & Singhal G S, J *Photochem Photobiol*, **19** (1993) 19-24.

156 Foyer C H, Dujardyn M & Lemoine Y, *Plant Physiol Biochem*, **27** (1989) 751-760.

157 Hodgson R A J & Raison J K, *Planta*, **183** (1989) 222-228.

158 Halliwell B, *New Phytol*, **73** (1989) 1075-1086.

159 Takahama U, *Plant Cell Physiol*, **23** (1982) 859-864.

160 Takahama U, *Plant Physiol*, **71** (1982) 598-601.

161 Whitmarsh J, Samson G & Poulson M, (See ref. 25) 1994, pp 75-94.

162 Chow W S, Osmond C B & Huang L K, *Photosynth Res*, **21** (1989) 17-26.

163 Adir N, Schochat S & Ohad I, *J Biol Chem*, **265** (1990) 12563- 12568.

164 Hundal I, Virgin I, Styring S & Andersson B, *Biochim Biophys Acta*, **1017** (1990) 235-41.

165 Anderson J M & Aro E M, *Photosynth Res*, **41** (1994) 315-326.

166 Aro E M, McCaffery S & Anderson J M, *Plant Physiol*, **104** (1994) 1033-1041.

167 Schnettger B, Critchley C, Santore U J, Graf M & Krause G H, *Plant Cell Environ*, **17** (1994) 55-64.

168 Larcher W, *Naturwissenschaften*, **74**, (1987) 158-167.

169 Strasser R J, A Concept of Stress and Its Application in Remote Sensing, *Application of Chlorophyll Fluorescence*, edited by H K Deihtenthaler (Kluwer Academic Publisher, Netherlands) 1988, 333-337.

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Fire Behaviour of Wood Substitutes

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Experimental investigations are made to assess the fire behaviour of some of the innovative alternatives to wood. Relevant fire properties, namely, non-combustibility, fire propagation index, surface spread of flame classification and specific optical density of smoke generated are determined in accordance with existing standard methods. The salient results of fire behaviour of Gypsum plaster board, Glass reinforced gypsum board, Particle board, Rice husk particle board, Cement bonded particle board and Extruded PVC structural foam obtained are compared with that of wood. The suitability of these materials from fire safety point of view as substitutes to wood for a particular use inside the buildings are discussed.

Introduction

Wood is an important building materials used in numerous applications such as door, window, flooring, partition, ceiling and furnitures. Wood is forest based product. Presently about 26 million cubic meters of wood is produced per annum from the forests in India[1]. Demand for wood in the housing sector including furniture is about 25 per cent of the total requirement of timber, presently being fulfilled by cutting trees resulting in ecological imbalance and loss of natural resources and habitation. The cost of wood consumed in building varies from 10- 30 per cent of the cost of building depending upon the extent of its utilization[2]. Though it is not easy to develop man made material which could substitute wood in all respect viz. warmth, aesthetics, textural and colour variety and structural qualities but there is a dire need to replace wood by suitable substitutes in building industry. With this background in a view some materials e.g. particle boards, fibre boards, hard boards, rice husk particle boards, cement bonded particle boards, plastic and polymer composites, etc. have been developed as wood substitutes. Besides these innovative material, many more products like glass reinforced gypsum board, gypsum plaster board have been reported as partial wood substitutes[3]. Fire statistics reveal that fire claims the life of few lakhs of people and destroy property worth billion of rupees every year[4]. Uncontrolled accidental fire still prevails in the modern world. But there must be cause behind every fire. A prime cause of this hazard is the use of natural and synthetic combustible materials in the interior of the building. A fire is a result of involvement of combustible materials which when ignited, release heat into the compartment, thereby raising the temperature of other materials at a distance[5]. These materials also get heated up to their ignition temperatures and start burning. Different combustible materials thus get involved successively. Thus a fire grows in size and spreads inside the building through combustible materials apart from hot gases and radiation.

The rate at which a fire grows is critical and depends upon the type of the materials used. If the materials are used such that these do not get ignited easily, do not spread flames over their surfaces rapidly, do not generate significant heat as they burn, they would not cause extensive damage. It is very important therefore, that materials used are evaluated for their likely fire behaviour and only those found suitable are recommended for use. A wide variety of wood substitute materials are available to users, architects and designers which can be used for a particular situation within a building. For selecting suitable wood substitutes for a particular use inside the building it is very important that these materials are evaluated for their likely fire behaviour and their

fire behaviour is to be compared with the fire behaviour of wood, for which these are substitutes.

The wood substitutes materials of which fire behaviour compared here are:

(i) Gypsum Plaster Board
(ii) Glass Reinforced Gypsum Board
(iii) Particle Board
(iv) Rice Husk Particle Board
(v) Cement Bonded Particle Board
(vi) Extruded PVC Structural foam

The brief description about the above materials including their uses is as follows.

Gypsum Plaster Board[6]: Gypsum plaster boards are very popular in several countries. Gypsum plaster is the main raw material for the manufacture of plaster boards. Gypsum as low as 70 per cent purity can be used for this purpose. The board is known for its light weight and thermal insulation. Principle uses of such boards are for false ceilings, light weight partitions and as dry surfacing materials for walls.

Glass Reinforced Gypsum Board[7]: Glass reinforced gypsum board which can be used as partial substitute of wood has been developed. The raw materials for the process are plaster of Paris and glass fibres in the form of rovings. The materials is insect proof and rot proof and has better dimensional stability in normal atmosphere. All wood working process such as sawing, drilling, milling, can be utilized for the material. Glass reinforced gypsum board could be used for structural partitions in school buildings for floor and roof slabs.[7]

Particle Boards[8,9]: The most common type of particle board is made from wood chips obtained from forest thinnings and timber work from peeler cores, shortings and mill waste and using resin binder. Particle boards are available in different sizes. It presents a uniform and smooth surface and can be cut and nailed. All other properties make its an ideal material for many interior application in buildings. Particle boards could be used for door shutters, Partitions, dividers, ceilings, paneling, flooring including cavity floors, in built cabinets and shelves, kitchen and living room furniture, thermal and acoustic insulation[8,9].

Rice Husk particle Board: For the first time one board from rice husk, suited to Indian climate and requirement, have been developed as an alternative to wood based particle boards. Rice Husk Particle Board is essentially made of rice husk particles bounded together by a resin. The Rice Husk Particle Board is termite resistant, decay resistant and rodent resistant. These boards have technically superior strength, dimensional stability, screw and nail holding capacity. The boards have been widely used to manufacture doors, partitions and false ceilings[10].

Cement Bonded Particle Board: The recent trend is to develop materials using industrial wood wastes and residues, soft woods, fast growing wood species, agricultural residues and natural fibres in inorganic matrices like cement etc. Investigations carried out using cement as matrix, has resulted in the development of process technologies for the production of Cement Bonded Particle Boards. Physico-mechanical properties, resistance to water/wet conditions of these boards are comparable with traditional materials. Cement Bonded Particle Boards are used for various applications in buildings like paneling, partitioning, cladding, false ceiling and wall lining[11].

Extruded PVC Structural Foam: Extruded PVC Structural Foam can either be produced by a free foam process, which produces a profile with a relatively thin skin, or by a controlled foam process where the profile does have a well defined integral skin. Extruded PVC Structural Foam can be used as a wood substitute for applications such as cladding, paneling, ceiling and wall lining[12].

Fire Behaviour

The fire behaviour of material is assessed by determination of fire properties. The fire properties are determined in order to obtain the following information.

* Can a material burn?
* Can it be ignited by small sources of flame?
* What is its contribution to the growth of a fire?
* What is its tendency to spread flames over the surface? and
* How dark is the smoke generated by it?

The relevant fire properties of materials that should be considered are as follows:

(I) Non-combustibility
(II) Ignitability
(III) Fire Propagation Index
(IV) Surface Spread of Flame Classification and
(V) Specific Optical Density of Smoke Generated.

For certain materials fire properties such as Flammability. Fire Retardancy, Toxicity, Fire Resistance and other fire behaviour properties are also determined.

The determination of the above fire properties is carried out by using standard apparatuses. These apparatuses have been developed in different countries and have been adopted by them for the purpose.

Non-Combustibility[6,13-14].

Non-combustibility is the property of a material to withstand high temperature without ignition.

Non-combustibility of a material is determined to ascertain whether it will contribute directly to fire development or not. It is intended for selection of materials, which while not completely inert can produce only a limited amount of heat and flame when exposed to a temperature of approximately 750°C.

The purpose of Non-combustibility test is to identify those materials which are safe under all circumstances. It is a test of the "go, no-go" type and classifies materials as "Combustible" or "Non-combustible".

The method of determination of Non-combustibility is specified in Indian Standard. IS:3808-1979. The test specifications are shown in Table 1. The test apparatus consists of an electric tubular furnace having inner diameter of 75 mm and length 150 mm. A resistance wire inside the furnace is wound in such a way that a temperature of 750°C is obtained (as measured by the thermocouple placed 10 mm away from the inner surface of the furnace) in the central part of the furnace. The cylindrical specimen of a material is exposed into the centre of the furnace and the temperatures are recorded continuously for 20 min. at three locations i.e. in the specimen centre, on the specimen surface and in the furnace. The duration of sustained flaming above 5 s and the mass loss is also recorded.

The average rise of temperatures above the furnace temperature, duration of sustained flaming and mass loss of the specimen of a material is computed. If these values are within specified limits, the material is designated "Non-combustible". Otherwise it is designated "Combustible". Non-combustibility test results. of wood and some wood substitutes are summarized in Table 6.

Table 1 — Non combustibility Test Specifications as per IS: 3808

Specimen	Five cylindrical specimens, diameters 45 mm, height 50 mm, volume 80 cu. cm.
Specimen Position	Vertical in specimen holde
Radiation Source	Electric furnace heated to 750 deg C (as indicated by furnace thermocouple which is located at mid height and at 10 mm from the inner wall of the furnace)
Test Duration	Twenty min.
Conclusions	(I) A material is designated "Non-combustible" if none of the five specimens on average (i) cause a temperature rise of more then 50 deg C (as measured by thermocouples in the specimen centre, on the specimen surface and in the furnace) (ii) burn longer than 20 s (iii) Suffer a muss loss of more than 50 percent (II) A material is designated "Combustible" if any/all the requirements for "Non-combustible" are not met.

The non-combustible materials can be considered safe materials from fire behaviour aspects as they are expected not to contribute significantly to a fire and can be used in any situation within a building. But the use of combustible materials in buildings is unavoidable. Since combustible materials burn and contribute to growth and spread of fire. It is essential to know the behaviour of these materials in case of a fire. Selection of materials for use in different situations within a building, from combustible materials, is made on the basis of their other fire properties such as Ignitability. Fire Propagation, Surface Spread of Flame. Specific Optical Density of Smoke generated etc.

Ignitability[15]

Ignition is the onset of combustion. The purpose of ignitability test is to determine the ease with which combustible materials can be ignited from a small source of heat. The test specifications as per BS

Table 2 — Ignitability Test specifications as per BS 476: Part 5

Specimen	Three specimens, 228 mm x 228 mm
Specimen Position	Vertical
Ignition Source	A small burner with flame length of 10 mm inclined at 45, the tip of which is located at 3 mm from the central point of the face of the specimen.
Test Duration	10 s
Conclusions	(I) Classification 'P' (Not Easily Ignitable) if none of the specimens flame for more than 10s after removal of the flame and burning of the specimen does not exceed to an edge.
	(II) Classification 'X' (Easily Ignitable) if the requirements for 'P' are not met

Table 3 — Fire propagation Test Specifications as per BS 476: Part 6

Specimen	Three specimens of 225 mm x 25 mm x max. 50 mm.
Specimen Position	Vertical
Radiation/Ignition Source	(I) Gas pipe burners with 14 jects of 1.5 mm I.D. at 12.5 mm centre
	(II) Two 1000 W electric heating elements with variable output (1800) W after 2 min 45 s and 1500 W after 5 min till the end of the test.
Test Duration	Twenty min.
Conclusions	Determination of
	1. Sub index i_1 and
	2. Fire propagation Index I

476:Part 5 are shown in Table 2. The test is carried out by exposing the specimen to a 10 mm long flame for 10 s. A note is made of the extent of flaming during the application of the pilot flame and for 10 s immediately thereafter.

Ignitability test helps to classify materials as "Easily Ignitable" or "Not Easily Ignitable" depending on whether or not a material flames beyond a specified distance in a fixed time interval. This test enables hazardous materials to be separated from non-hazardous materials on the basis of their ease of ignition. Materials which fail this test should not be used in any exposed situation as they could easily lead to the start of a fire.

Ignitability test results of wood and some wood substitutes are summarized in Table 6.

Fire Propagation Index[16-17]

The fire Propagation Index of materials can be used to identify the likely hazard of lining materials in terms of their tendency to contribute towards the growth of fire inside the buildings. A material of higher Fire Propagation Index is considered to contribute more than the one of a lower Fire Propagation Index. Thus by comparison of the Fire Propagation Indices of different materials for the interior of building, it is possible to identify safer materials and the performance of different materials can be ascertained relative to each other.

The Fire Propagation Index is determined using the Fire Propagation Apparatus and by following the procedure specified in BS 476 : Part 6. The test specification are shown in Table 3. A calibration run is conducted by exposing a non combustible board of specified properties to the 14 jets of a gas pipe burner at a distance of 3 mm. The two electric heating elements with a, total output of 1800 W are switched on after 2 min 45 s. Their output is reduced to 1500 W after 5 min and maintained constant till the end of the test. The flue gas temperatures are measured by two thermocouples inserted in the annular space between chimney and cowl. Another experimental run is conducted with the specimen of a material keeping the test conditions same as that for calibration run and time temperature data is recorded. The Fire Propagation Index is computed as follows from these data.

$$I = \underbrace{\frac{\sum_{0.5}^{3} \theta_m - \theta_c}{10\,t}}_{i_1} + \underbrace{\frac{\sum_{4}^{10} \theta_m - \theta_c}{10\,t}}_{i_2} + \underbrace{\frac{\sum_{12}^{20} \theta_m - \theta_c}{10\,t}}_{i_3}$$

1/2 min interval 1 min interval 2 min interval.

$I = i_1 + i_2 + i_3$

where, I is the Fire Propagation Index.

i_1, i_2, i_3 are the sub-indices for the three time components,

θ_m is the temperature rise recorded for the material at time t

θ_c is the temperature rise recorded for non- combustible standard at time t and

t is the time in min from the beginning of the test.

The Fire Propagation Index is the sum of three sub-indices i_1, i_2 and i_3. Higher the value of the sub index i_1, or the Fire Propagation Index I, higher is the likely contribution of the material to fire. The first subindex i_1 and the Fire Propagation Index I of wood and wood substitutes materials are summarized in Table 6.

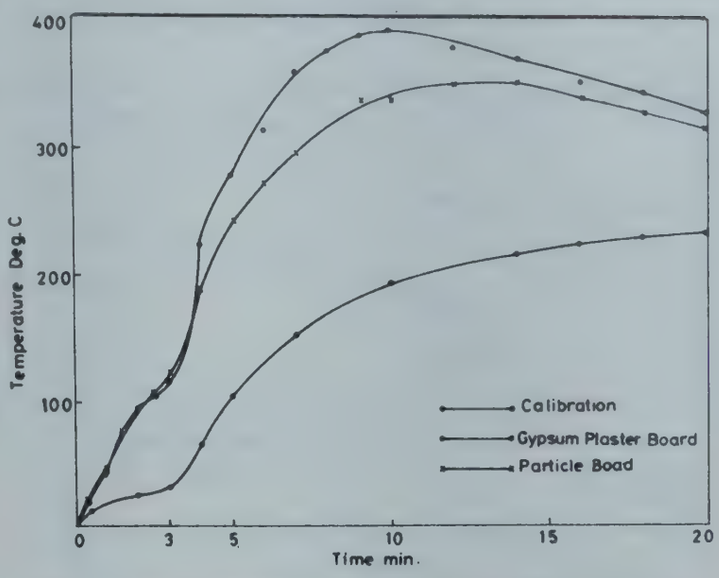

Fig. 1. Time-Temperature curves for Woods (Kail Wood and Deodar Wood) and Calibration run obtained during the Fire Propagation Test.

Surface Spread of Flame Classification[18]

Materials used for walls and ceilings have a significant effect on the way in which fire spreads. In particular, it is essential that the flame spread be negligible in evacuation spaces and means of escape. The Surface Spread of Flame test was devised to determine the burning characteristics of materials by considering the flame spread over their surfaces.

The classification of materials for Surface Spread of Flame is determined using the apparatus described in British Standard BS : 476 : Part 7. The test specifications are shown in Table 4.1 and Table 4.2. The specimen is exposed to the radiant panel and; in addition, the pilot flame is applied during the first minute of the test.

The distance of flame spread is recorded at the end of 1.5 minute and measurement of flame spread against time are continued up to a total duration of 10 min, unless the flame has reached the far end of the specimen in less than 10 min.

The material is then classified in one of the four classes i.e. Class 1 / Class 2 /Class 3 /Class 4 according to the test performance. Class 1 material have the lowest rate of flame spread and class 4 has the highest. Thus a selection of materials can be made depending on their Surface Spread of Flame Classification.

Table 4.1 — Surface Spread of Flame Test Specifications as per BS 476: Part 7

Specimen	Six specimens 885 mm x 270 mm x max. 50 mm
Specimen Position	Vertical, longitudinal axis (885 mm). at right angle to the radiant panel.
Radiation/Ignition Sources	(i) Gas fired radiant panel with radiation intensity of 32.5 KW/m^2 at 75 mm from the radiant panel surface (ii) Gas pilot with 100 mm flame length below the specimen on the same side as the radiant panel.
Test Duration	Ten min.
Conclusions	Classification in Class 1/Class 2/ Class 3/Class 4 depending on test performance (as shown in Table 4.2)

Table 4.2 — Classification of Spread of Flame

Classification	Flame Spread at 1.5 Min		Final Flame Spread	
	Limit (mm)	Tolerance for one specimen (mm)	Limit (mm)	Tolerance for one specimen (mm)
	(mm)	(mm)	(mm)	(mm)
Class 1	165	25	165	25
Class 2	215	25	465	45
Class 3	265	25	710	75
Class 4	Exceeding the limits for Class 3			

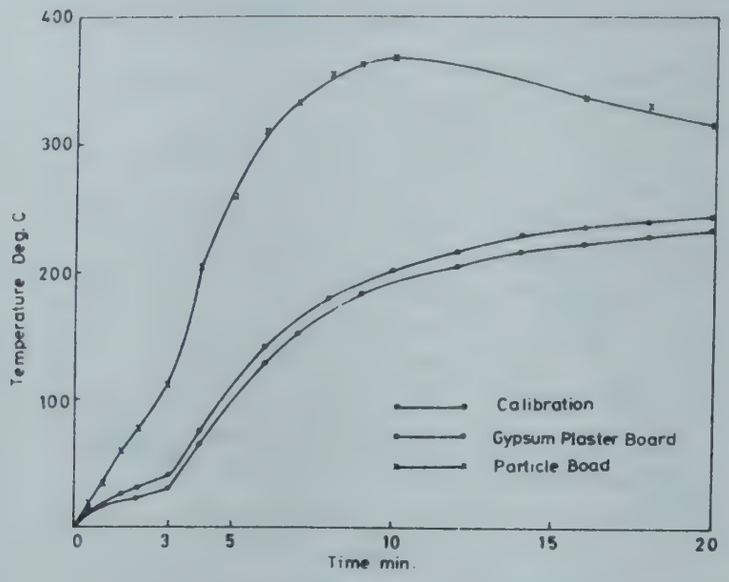

Fig. 2. Time-Temperature curves for Gypsum Plaster Board, Particle Board and Calibration run obtained during the Fire Propagation Test.

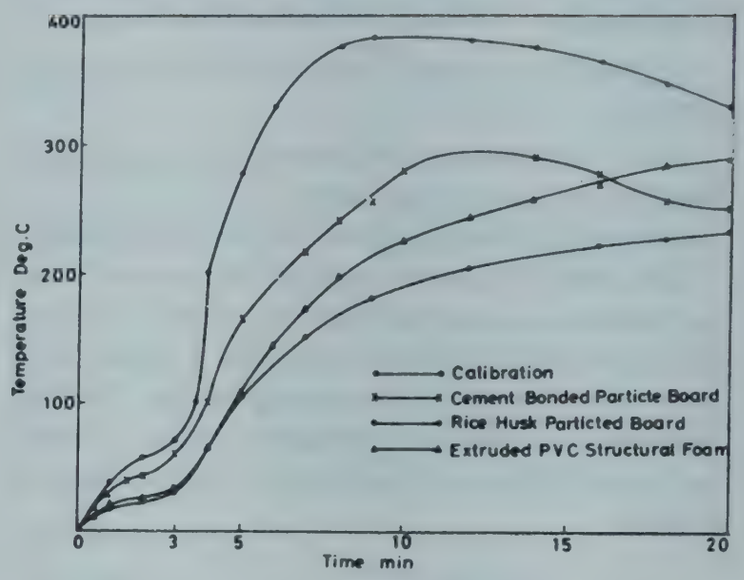

Fig.3. Time-Temperature curves for Rice Husk Particle Board, Cement Bonded Particle Board, Extruded PVC Structural Foam and Calibration run obtained during the Fire Propagation

The Surface Spread of Flame Classification of wood and some wood substitutes are summarized in Table 6.

Specific Optical Density of Smoke Generated[19-20]

Smoke results from incomplete combustion. It is a dispersion of solid or liquid particles in a carrier gas consisting of combustion gases and air. The level of smoke development depends on numerous factors such as the source of ignition, oxygen availability and the constitution and properties of combustible lining materials used in the interior of a buildings.

Smoke poses a danger to human life, particularly in the initial phases of a fire, due to the loss of orientation caused by sight obscuration. This can lead to panic and irrational behaviour which make escape impossible with fatal results. Smoke also hinders the fire brigade frequently making it impossible to rescue victims and to locate and effectively fight the seat of the fire.

The Specific Optical Density of Smoke is determined using the Smoke Density Chamber and by following the procedure specified in ASTM662. The test specification are shown in Table 5. During the test, the specimen is exposed to different modes. In one mode (Smoldering), the specimen is exposed to radiant heat alone; while in the other (Flaming), the specimen is exposed to radiant heat as well as flames. In both the modes, the smoke generated by the specimen is allowed to accumulate inside a closed cham-

Table 5 — Specific Optical Density of Smoke Test Specifications as per ASTM — E 662

Specimen	At least six specimens.76 mm x 76 mm x max 25 mm. three specimen for smouldering exposure mode and three specimen for flaming exposure mode.
Specimen Position	Vertical, in front of radiation source.
Test Chamber	Smoke Density chamber with internal dimensions 914 mm x 610 mm x 914 mm
Radiation/Ignition Sources	(i) A circular furnace of 76 mm diameter opening with radiation intensity of 2.5 W/cm^2 is positioned vertically (Smouldering conditions).
	(ii) Multiple tube gas burner located 6.4 mm away and specimen (Irradiation and application of the flame for flaming conditions)
Photometric System	A provision of light source with optics. A 914 mm long vertical light beam and photosensitive element.
Test Duration	Maximum twenty min.
Conclusions	Determination of Maximum Specific Optical Density of Smoke under
	1. Smouldering condition and
	2. Flaming condition

Table 6 — Fire Performance characteristics of Wood & Wood substitutes

Material	Test Results						
	Non-cumbustibility	Ignitability	Fire Propagation index		Flame spread class	Smoke Density, D_m	
			i_1	I		Flaming	Non-Flaming
Wood							
Kail Wood+ 12 mm, 495 kg/cu.m	C	P	16.14	14.15	4	288	329
Deodar Wood+ 12mm, 600 kg/cu.m.	C	P	17.00	36.00	4	249	318
Wood Substitutes							
Glass Reinforced Gypsum Board 12.5mm, 1200 kg/cu.m.	NC	-	-	-	-	-	-
Gypsum Plaster Board 12mm, 800 kg/cu.m	C	P	2.33	4.07	1	14	31
Particle Board+ 12mm, 400kg/cu.m	C	P	14.21	36.52	3	262	410
Rice Husk particle++ Board 12mm, 830 kg/cu.m.	C	P	10.30	35.00	3	150	272
Cement Boarded Particle Board 15mm, 1360 kg/cu.m.	C	P	0.87	4.37	1	25	8
Extructed PVC Structural Foam 10mm, 580 kg/cu.m.	C	P	7.10	16.10	1	561	374

Legends: NC — Non-combustible. C — Combustible. P— Not Easily Ignitable
i_1 — sub-index, I — Fire Propagation Index

Class 1 — Surface of very low flame spread
Class 3 — Surface of medium flame spread
Class 4 — Surface of rapid flame spread
DM — Maximum specific optical Density of smoke Generated

+ Ref 22
++Ref 21

ber and percent transmittance across a light path is measured.

The results are expressed as Maximum Specific Optical Density (Smouldering and Flaming). Higher the Maximum Specific Optical Density, higher is the effect of smoke from the material in reducing visibility and hampering escape. Thus a selection of material to be used in the interior of a building can be made on the basis of their Specific Optical Density of Smoke generated.

The Maximum Specific Optical Density of Smoke Generated by wood and some wood substitutes are summarized in Table 6.

Results and Discussions

For making a proper choice of wood substitutes materials from the fire safety point of view. The fire behaviour of these materials can serve as a useful guide. Also the comparison of their fire behaviour with the fire behaviour of material for which they are the alternatives i.e. for wood is important from fire safety purposes.

Fire behaviour of wood and wood substitutes is assessed using the standard apparatuses for the assessment of fire properties viz. Non-combustibility, Ignitability, Fire Propagation Index, Surface Spread of Flame Classification and Specific Optical Density of Smoke Generated: in which the specimen of materials are subjected to simulated conditions of fire exposure. Behaviour of these materials is observed and the desired characteristics is measured.

As different wood and wood substitute materials are exposed to the same conditions, performance of these materials can be compared and a relative ranking can be obtained. It is thus possible to judge which wood substitute material perform better than wood and indiscriminate use of other wood substitute materials can be avoided.

The results of experimental investigations on the specimens of Kailwood. Deodar Wood, Glass Reinforced Gypsum Board, Gypsum Plaster Boards, Particle Board, Rice Husk Particle Board, Cement Bonded Particle Board and Extruded PVC Structural Foam for the determination of the relevant fire properties are summarized in Table 6.

The Kailwood and Deodar wood are graded as "Combustible" by Non- combustibility test. They are classified as "Not Easily Ignitable" by Ignitability test. Fig. 1 shows the time- temperature curves for Kailwood and Deodar Wood and calibration run obtained on Fire Propagation Test. The temperature rise is significant over that for calibration run for both Kailwood and Deodar Wood. The computed sub-index i_1 for Kailwood and Deodar wood is 16.14 and 17.00 respectively; while Fire Propagation Index I is 41.15 and 36.00 respectively. The classification of Kailwood and Deodar Wood for the Surface Spread of Flame determined in accordance with BS: 476 Part 7 is Class 4 i.e. rapid flame spread. The values of the Maximum Specific Optical Density of Smoke Generated by Kailwood and Deodar wood for flaming exposure mode is 228 and 249 while that for non-flaming (Smouldering) exposure mode is 329 and 318 respectively.

The Glass Reinforced Gypsum Board is graded as "Non- combustible" by Non-combustibility test in accordance with IS 3808:1979. As the non-combustible materials are considered safe from fire behaviour aspects as they are expected not to contribute significantly to the development of fire: Glass Reinforced Gypsum Board can be used in any situation within the building and considered as a substitute of wood for particular application within the building. Also the non-combustible materials need not always be evaluated for other fire properties viz. Ignitability, Fire Propagation Index, Surface Spread of Flame classification and Specific Optical Density of Smoke Generated, the Glass Reinforced Gypsum Board is not evaluated for these properties.

The Gypsum Plaster Board is graded as "Combustible" and "Not Easily Ignitable" by Non-combustibility and Ignitability test respectively. The time-temperature curve of Gypsum Plaster Board (Fig.2) shows that the temperature rise is not significant over the temperature rise for calibration run. The computed value of sub-index and Fire Propagation Index is 2.33 and 4.07 respectively. These values are much less than that for wood. The Surface Spread of Flame Classification of Gypsum Plaster Board is Class 1 i.e. the surface of very low flame spread. The values of Specific Optical Density of Smoke for flaming exposure mode and non-flaming exposure mode is 14 and 31 respectively. The fire behaviour of Gypsum Plaster Board is Superior to wood in respect of the Fire Propagation Index, the Surface Spread of classification and the Specific Optical Density of Smoke Generated. Therefore, Gypsum Plaster Board can be used as a wood substitute within the building.

Particle Board 12 mm thick and of density 400 kg/cu.m. is "Combustible" and Not Easily Ignitable". The time-temperature curve for Particle Board (Fig.2) shows the temperature rise over that for calibration run is similar to that for wood (Fig.1). The values of sub index i_1 and Fire Propagation Index is 14.21 and 36.52. While Surface Spread of Flame Classification is Class 3. The Specific Optical Density of Smoke Generated for flaming exposure mode is 262 and for non-flaming exposure mode is 410. The fire behaviour of Particle Board is similar to

wood in respect of Non-combustibility. Ignitability, Fire Propagation Index and Specific Optical Density of smoke Generated. It is superior to wood in respect of Surface Spread of Flame Classification. Therefore, the use of Particle Board as replacement of wood is considered inside the building.

Rice Husk Particle Board 12 mm thick and of density 830 kg/cu.m. is graded as "Combustible" and "Not Easily Ignitable" as per Non- combustibility and Ignitability test. Its Fire Propagation Index is 35.00 while the sub-index is 10.30. The time temperature curve obtained during Fire Propagation Test is shown in Fig.3. Its Surface Spread of Flame Classification is Class 3 while the values of Specific Optical Density of Smoke Generated for flaming exposure mode and non flaming exposure mode is 150 and 272 respectively. The fire behaviour of Rice Husk Particle Board[21] is superior to wood in respect of Surface Spread of Flame Classification and Specific Optical Density of Smoke Generated. Hence it can be used as alternative to wood inside the buildings.

Cement Bonded Particle Board is "Combustible" and "Not Easily Ignitable". The Fig. 3 shows that temperature rise of Cement Bonded Particle Board is not significant over that for calibration run. The values of i_1. and I is 0.87 and 4.37 respectively, which is very less as compared to that for wood. Its Surface Spread Classification is Class 1 which is also better than wood (Class 4). It is also superior to wood in respect of Specific Optical Density of Smoke Generated. Therefore, fire behaviour of Cement Bonded Particle Board is superior to that of wood and hence it can be used as replacement of wood inside the building.

Extruded PVC Structural Foam is graded as "Combustible" and "Not Easily Ignitable" as per Non-combustibility and Ignitability test. The behaviour of its temperature rise over the temperature rise of calibration run in accordance with BS 476 : Part 6 is shown in Fig.3. The values of i_1 and I is 7.10 and 16.10 respectively, which is better than that for wood. Extruded PVC Structural Foam (Class 1) is also superior to wood in respect of Surface Spread of Flame Classification. The values of Specific Optical Density of Smoke Generated for flaming exposure mode is 561 and for non-flaming exposure mode is 374. Which is more than that for wood. The fire behaviour of Extruded PVC Structural Foam is superior to wood in respect of Fire Propagation Index and Surface Spread of Flame Classification; while it is inferior to wood in respect of Specific Optical Density of Smoke Generated. Therefore, it should be used as wood substitute in situations where the smoke generation would not have serious adverse implications.

Conclusions

For making a proper choice of wood substitute materials, from the fire safety point of view, the Fire Behaviour of these materials and its comparison with that of wood, can serve as a useful guide.

The Wood Substitute, Glass Reinforced Gypsum Board being 'Non- combustible' would not contribute to the growth and spread of fire and is considered safe from fire behaviour point of view. It can be used in any situation inside the building.

The fire behaviour of Gypsum Plaster Board and Cement Bonded Particle Board is superior to wood in respect of Fire Propagation Index, Surface Spread of Flame Classification and Specific Optical Density of Smoke Generated. Therefore, these materials are better alternative to wood.

The fire behaviour of Particle Board and Rice Husk Particle Board is similar to that of conventional wood, therefore these materials are suitable for application in place of wood inside the buildings.

The Fire behaviour of Extruded PVC Structural Foam is superior to wood in respect of Fire Propagation Index and Surface Spread of Flame Classification, but inferior in respect of Specific Optical Density of Smoke Generated. Therefore, its use as an alternative is considered in situations where smoke generation would not have any adverse implications.

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References

1 Thomas P T, Babu B R S & Neelakandhan K, *Bull Material Sci* **16** (1993) 73.

2 Gupta S C, *National Seminar on New Materials in Building Industry*, New Delhi, Sept. (1993) II-1.

3 Singh Manjit, Verma C L, Garg Mridul, Handa S K & Kumar Rakesh, *Res Ind*, **39** (1994) 55.

4 Phatak B, *NFSC Journal* 1 (2) (1995) 14.

5 *Non-combustibility of Materials, Building Research Note* (Central Building Research Institute, Roorkee) 78 (1990).

6 *Gypsum as a building material, Building Research Note* (Central Building Research Institute, Roorkee) 15 (1988).

7 *Building Materials and Components* - Technology for *Developing Countries* (Tata Mc Gram-Hill Publishing Company Ltd., New Delhi) (1990).

8 *Particle Board and its Use in Building Building Research Note* (Central Building Research Institute, Roorkee) 55 (1986).

9 Pandey S N, Dey R N & Dey A, *Workshop on Polymer Composites as Substitutes for Conventional Building Materials*, New Delhi, Oct 3 (1988).

10 Narayanswamy S T, *Rice Husk Particle Board - An Innovative Alternative to Wood Particle Board, Souvenir of National Symposium on Substitutes for Wood in Buildings* (Central Building Research Institute, Roorkee) Dec. (1991).

11 Agarwal S P & Agarwal L K. *Cement Bonded Composite Materials, Souvenir of National Symposium on Substitutes for Wood in Buildings* (Central Building Research Institute, Roorkee) Dec. (1991).

12 Hitch M J & Rolph D C, *PVC Foams - Their Use and fire behaviour; Fire and Cellular Polymers*, (Elsevier Applied Sciences Publishers Ltd., London) (1986) 222.

13 *Standard Terminology Relating to Fire Standards*. ASTM *designation E 176-819. 1988 Annual Book of ASTM Standards*. (American Society for Testing and Materials, Philadelphia) 14(04.07), (1988).

14 *Method of T for Non-combustibility of Building Materials*:IS 3808-1979 (Bureau of Indian Standards. New Delhi) (1979).

15 *Fire Tests on Building Materials and Structures. Part 5. Ignitability Test for Materials BS 476: Part 5: 1968.* (British Standards Institution, London) (1968).

16 *Fire Tests on Building Materials and Structures*. Part 6. *Method of Tests for Fire Propagation of Products*, BS 476: Part 6; 1981 (British Standards Institution, London) (1981).

17 *Fire Propagation Index of Lining Materials, Building Research Note* (Central Building Research Institute, Roorkee) 74 (1990).

18 *Fire Tests on Building Materials and Structures*. Part 7. *Method for classification of the Surface Spread of Flame of Products. BS 476 : Part 7: 1987.* (British Standards Institution, London) (1987).

19 *Standard Test Method for Specific Optical Density* of *Smoke Generated by Solid Materials, ASTM Designation E 662-1983. 1988 Annual Book of ASTM Standards* (American Society of Testing and Materials. Philadelphia) 14 (04.07) (1988). 523-544.

20 *Smoke Generation by Lining Materials. Building Research Note*. (Central Building Research Institute, Roorkee) 76, (1991).

21 Bhatnagar S K, *Fire and Rice and Rice Husk Particle Board. Fire Materials*, 18(1994) 51-55.

22 Sharma Sunil K, *Extruded PVC Building Products and Their Fire Performance, Workshop on Polymer Composites as Substitute for Conventional Building Materials*, New Delhi, Oct. 3(1988).

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Synthesis and Applications of Oil-modified Polyesteramide Resins for Surface Coatings

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Polyesteramide resins, suitable for coating applications, have been synthesised, using two different oils, viz: a non traditional, nonoxidising type, pilu fat (*Salvadora Oleoides*) and a traditional oxidizing type, dehydrated castor oil (DCO). N, N- bis-(2-hydroxyethyl) fattyamides (HEFAs) have been prepared by aminolysis of both pilu oil and DCO with diethanolamine using zinc oxide as a catalyst. HEFAs were reacted with isophthalic acid in varying molar ratios to obtain a series of hydroxy terminated polyesteramides (HTPEAs). Coating compositions from these resins were formulated by incorporation of butylated melamine formaldehyde (BMF) resin in two different ratios. The baked film properties of these resins have been evaluated. Furthermore both pilu fat and DCO can be used as components of industrial stoving finishes. Pilu fat, being nonoxidising type, can replace traditionally used coconut oil in such applications.

Introduction

Baking finishes based on alkyd/amino resin systems are very widely used for industrial applications, especially for original equipment manufacturer (OEM) finishes[1]. The type of alkyd resins used in such systems include nonoxidising short oil alkyds generally based on castor oil or coconut oil depending upon finished product requirements. Butylated urea formaldehyde or melamine formaldehyde are used in conjunction with such alkyds as cross-linking resins. Alkyd based coating systems are limited to a certain extent by their relatively poor resistance to hydrolysis particularly by alkali[2]. This is believed to be due to the presence of ester linkages in their polymeric backbone, which are prone to hydrolysis[3]. Polyesteramide resins containing sufficient amide linkages are known to improve water and chemical resistance properties of their films[4,5,6,7].

In the present work, non-oxidizing type polyesteramide resins derived from pilu fat (*Salvadora Oleoids*) have been employed as a component of a baking system in conjunction with butylated melamine formaldehyde resins to improve upon chemical properties of the cured films. The scheme for preparation of polyesteramide is shown in Fig. 1.

Materials and Methods

While refined pilu fat and DCO have been locally procured, the other chemicals zinc oxide, isophthalic acid, xylene, methanol and butanol were (lab reagent grade). Butylated melamine formaldehyde resin (BMF) code No. 310 was procured from M/s Synthetics and Polymers Ltd. and was used without any modification. Table 1 depicts the characteristics of BMF resin. The acid value, colour, viscosity, nonvolatile content, drying time, scratch resistance, flexibility and adhesion were determined as per Indian Standard methods[8,9]. Resistance towards acid, alkali, water and xylene were determined as per standard methods described in the literature[10].

The infrared spectrum of polyesteramide was recorded using Shimaru spectrophotometer. The flexibility was measured using 1/4" and 1/8" conical mandrel. The films were applied on mild steel panels (6" x 4") and (6" x 2") and mechanical properties were studied as per Indian Standard Specifications[8].

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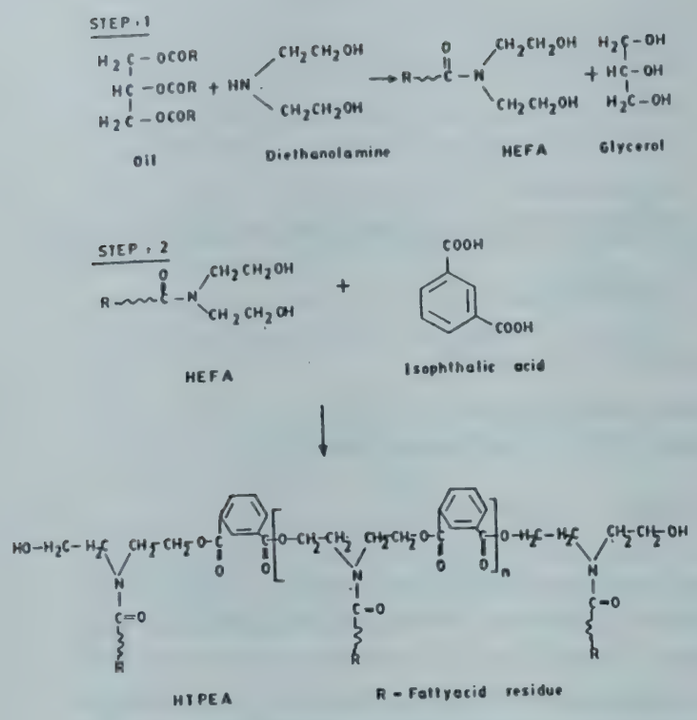

Fig.1 — Scheme for preparation of polysteramide

Table 1 — Characteristics of Butylated Melamine Formaldehyde resin (SYNPOL MF-310)

S. No.	Characteristic Properties	
1.	Percentage non-volatile	60
2.	Viscosity (Poise) (25 °C)	16
3.	Acid value (mg KOH/g)	02
4.	Mineral Spirit Tolerance	52
5.	Density (at 25 °C) (g/cm^2)	1.02

Impact resistance of films has been determined by falling weight type impact tester[10].

Experimental

Preparation of N, N-bis (2-hydroxyethyl) Fatty Amides (HEFA)

These diethanolamides were prepared directly from pilu fat and DCO according to the reported method[6,7,11-13]. The characteristics and fatty acid compositions of pilu fat and DCO used are shown in Table 2. Purified pilu fat/DCO (1.0 mole) was heated under nitrogen with diethanolamine (3.0 mole) at 200 °C with efficient stirring for 15 minutes, using zinc oxide (0.02 mole) as a catalyst. The progress of the

Table 2 — Characteristics and fatty acid compositions of DCO and Pilu fat

a) Characteristics

S. No.	Characteristic Properties	DCO	Pilu fat
1.	Acid value (mg KOH/g)	9.00	5.00
2.	Saponification value (mgKOH/g)	187.0	253.0
3.	Iodine value	149.0	7.0
4.	Hydroxyl value (mg KOH/g)	16.0	3.0
5.	Specific Gravity	0.94	0.91
6.	Refractive index (@ 30 °C)	1.438	1.428
7.	Colour (y+5R) (Lovibond)	11.0	6.0

b) Fatty acid composition (% by wt.)

S. No.	Fatty acid	DCO	Pilu fat
1.	Oleic	9.0	—
2.	Linoleic	83.0	—
3.	Linolenic	5.0	—
4.	Ricinoleic	3.0	—
5.	Caprylic	—	8.6
6.	Capric	—	5.3
7.	Lauric	—	52.8
8.	Myristic	—	32.0
9.	Palmitic	—	1.3

reaction was monitored with the help of thin layer chromatography (TLC), until the disappearance of the spot of oil was observed [6,13,14]. The fatty acid diethanolamides were purified from glycerol, excess diethanolamine and other water soluble impurities by washing its solution in diethyl ether with 15% aqueous sodium chloride solution, followed by distilled water. The characteristics of HEFAs are reported in Table 3.

Table 3 — Characteristics of HEFAs

S. No.	Characteristic properties	HEDA	HEPA
1.	Acid value (mg KOH/g)	4.00	3.00
2.	Hydroxyl value (mg KOH/g)	288.00	384.00
3.	Viscosity (@ 25 °C) (Poise)	5.00	9.00
4.	Colour (y+5R) (Lovibond)	12.00	9.00
5.	Specific gravity	0.96	0.98

Preparation of Hydroxy Terminated Polyesteramide (HTPEA)

These polyesteramides were prepared by reacting HEFAs (1.15 to 1.45 mole) with isophthalic acid. The reactants were heated with sufficient stirring under nitrogen at a temperature of 190±5 °C for about 3.5 hours. Water of the reaction was continuously removed in Dean-Stark moisture trap by azeotropic distillation using xylene as a solvent. The acid value of the reaction products was periodically checked to study the progress of the reaction. The condensation reaction was carried out until low acid values were obtained. Resultant resins were thinned to 60% solid using xylene as the solvent. In Table 4, the characteristics of HTPEAs are shown.

Preparation of Coating Compositions

Coating compositions were prepared by combination of BMF and different HTPEAs in two different ratios, viz. 4:1 and 3:1. The compositions were thinned to the required viscosity for application and the films were applied and baked at 150 °C. Various film properties were studied.

Results and Discussion

An attempt has been made to evaluate structure property relations and to study various applications of the coatings prepared from the polyesteramides. These coatings on application using brush, baked at 150°C produced hard, adherent and flexible coatings.

Table 4 — Characteristics of Polyesteramides

S. No.	Resin Code	Molar excess of HEFA	Viscosity* at 30°C (Poise)	Colour (Gardner)	Acid value mg KOH/g	Hydroxyl Value mgKOH/g	Specific gravity
1.	Pilu-15	0.15	3.4	14	14	41.04	0.96
2.	Pilu-25	0.25	3.0	14	12	65.0	0.95
3.	Pilu-35	0.35	2.7	13	9	86.72	0.96
4.	Pilu-45	0.45	2.25	13	8	104.21	0.97
5.	DCO-15	0.15	5.0	15	12	38.34	0.97
6.	DCO-25	0.25	4.70	14	10	61.18	0.96
7.	DCO-35	0.35	4.30	14	11	80.15	0.95
8.	DCO-45	0.45	4.00	13	8	99.43	0.95

* Viscosity of pilu polyesteramides is measured as 50% solution.

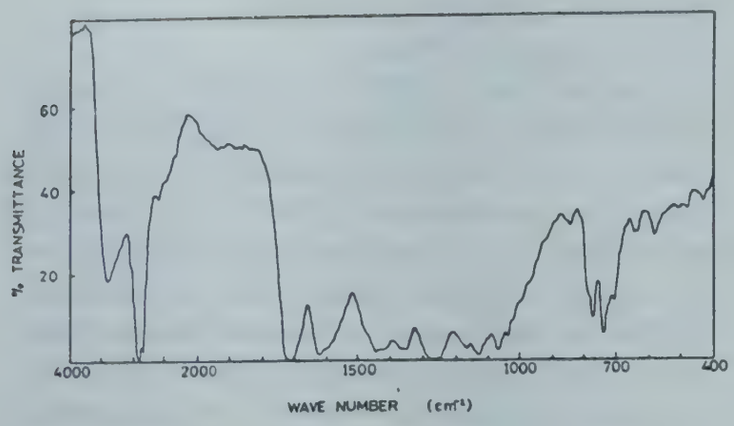

Fig.2 — IR spectrum of polysteramide (DCO)

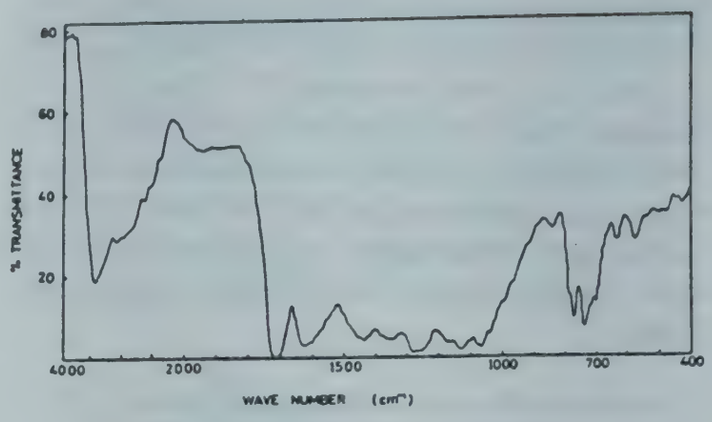

Fig.3 — IR spectrum of polysteramide (pilu)

Isophthalic acid has been used as acid component, since isophthalic esters have better resistance to hydrolysis than their phthalic anhydride counterparts[2,4-6]. Isophthalic acid based polymers on comparison with phthalic anhydride based polymers have high molecular weights[2] which give improved mechanical and chemical properties to their films[6,7].

From the results, it was found that the hydroxyl values of HTPEAs derived from both the oils increase with increase in molar excess of HEFA, the viscosity and colour of the resins decrease. The decrease in viscosity can be accounted for the lower molecular weight of polymers due to molar excess of hydroxyl groups over acid functions[10]. The lowering of colour intensity can be due to shorter processing time with increasing excess of HEFA. The structure of polyesteramide was confirmed from IR spectrum (Figs. 2 and 3). The absorption bands are at 3400 cm^{-1} (-OH group), 1740 cm^{-1} (ester group), 820 cm^{-1} (-C-N stretching), 1640 cm^{-1} and 1725 cm^{-1} (-C=O stretching), 1620 cm^{-1}, 1775 cm^{-1}, 1070 cm^{-1} and 740 cm^{-1} (aromatic moiety)[15].

Film Properties

In Table 5 various film properties of cured films of different polyesteramide compositions have been depicted. All the samples were tested for flexibility, adhesion, scratch hardness and solvent resistance. The samples passed flexibility test on 1/4" and 1/8" conical mandrel, which is expected of oil based coatings. All samples passed stripping test for adhesion. Scratch hardness increases with increase in hydroxyl value of HTPEAs. This may be due to the increase in crosslink density of films. Impact resistance decreases with increase in hydroxyl value. This might be due to excessive crosslink density of the films, leading to embrittlement. Further, coating compositions, containing more MF content show greater scratch resistance and lower impact resistance than those containing less MF content.

Furthermore tests for resistance against acid, alkali, water and solvent have been conducted of the surface coatings. It is seen that acid and alkali resistance increases with increase in hydroxyl content of HTPEA. All the samples show good water and solvent resistance.

Conclusions

The polyesteramide resins derived from both pilu fat and DCO can successfully be employed as components of industrial stoving finishes. It has been observed that the mechanical property, such as impact resistance, is a function of hydroxyl value of the resins and hence optimum level of excess hydroxy components should be used in synthesis of resins to achieve good balance between performance properties.

Acknowledgment

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References

1 Wicks, Z W, Jr. Jones, F N, Pappas, S P, *Organic Coatings : Science and Technology* (John Wiley & Sons, New York) Vol.2 (1994) 178.

2 Swaraj Paul, *Surface Coatings, Science and Technology* (John Wiley & Sons, New York) 1985 (Chap. 2) 133.

Table 5 — Baked Film Properties of Polyesteramides

S.No.	Resin Code		Impact Resistance ibs.		Scratch Hardness (kg)	Chemical Resistance			
			Direct	Reverse		2% HCl (200 hrs.)	2% NaOH (Pass)	Xylene (200 hrs.)	Water (200 hrs.)
1.	Pilu-15	4:1	175	175	1.0	P	1.45	P	P
		3:1	200	175	1.3	P	2.00	P	P
2.	Pilu-25	4:1	250	250	1.4	P	2.00	P	P
		3:1	225	200	1.6	P	2.25	P	P
3.	Pilu-35	4:1	250	250	1.6	P	2.30	P	P
		3:1	225	225	2.0	P	2.45	P	P
4.	Pilu-45	4:1	150	125	0.9	P	3.30	P	P
		3:1	125	100	1.2	P	4.00	P	P
5.	DCO-15	4:1	200	175	1.6	P	2.00	P	P
		3:1	275	250	1.4	P	2.25	P	P
6.	DCO-25	4:1	275	275	1.4	P	2.20	P	P
		3:1	200	150	1.7	P	2.45	P	P
7.	DCO-35	4:1	250	250	1.0	P	3.00	P	P
		3:1	225	200	1.2	P	3.15	P	P
8.	DCO-45	4:1	200	150	1.2	P	3.35	P	P
		3:1	175	150	0.8	P	4.10	P	P

3 Mannari, V M, Ph.D Dissertation, *Synthesis and applications of oil-modified polyesteramide resins for surface coatings*, Sardar Patel University, Vallabh Vidyanagar, 1995, 37.

4 Mark, H F, Bikales, N M, Overberger, C G & Menges, G, *Encyclopedia of Polymer Science and Engineering* (John Wiley & Sons, New York) **1**, 2nd Edn (1985) 652.

5 Oil & Colour Chemists Association, Australia, *Surface Coatings*, (Chapman & Hall, London) Vol. 1, Chap. 9 (1987) 95.

6 Raval, D A, Roy, T K & Mannari, V M, *J Sci Ind Res*, 55(1996), 263.

7 Roy, T K, Mannari, V M & Raval, D A, *J Sci Ind Res*, 55(1996), 971.

8 IS-197 (1967), *Methods of Sampling and Testing for Varnishes and Lacquers*, (First Revision, 1981) (Bureau of Indian Standards, New Delhi).

9 IS-354 revised (1976). *Indian Standard Methods of Sampling and Test for Resins and Paints*, (Bureau of Indian Standards, New Delhi).

10 Lambourne, R, *Paint and Surface Coatings, Theory and Practice*, (Ellis Horwood, Chichester) 1987, 616.

11 Varghese, T M & Krishnan, V, *J. Colour Soci.* **29** (Oct-Dec) (1990) 1.

12 Gast, L E, Schneider, W J & Cowan, J C, *J. Ameri Oil Chem Soc.* **43** (1996), 337.

13 Raval, D A & Mannari, V M, *Res & Ind*, 38(3)(1993) 129.

14 Varghese, T M & Krishnan, V, J. *Colour Soci.*, **29** (Jul-Sep)(1990) 1.

15 Urbanski, J, Czeriwinskim W, Janicka, K, Majevska, F & Zowall, H, *Handbook of Analysis of Synthetic Polymers and Plastics* (Ellis Horwood Ltd., Chichester) 1977, 234.

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Manufacture Of Aleuritic Acid From Seed Lac: Some Practical Considerations

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The industrial process for manufacturing aleuritic acid from seed lac poses certain problems like the long saponification period, need for reprocessing the crude product and the inevitable loss during this step. Some improvements are suggested to overcome these problems and get *threo* - aleuritic acid of 92% purity in an optimised yield of 23%. A GC assay procedure for determining its purity is developed.

Introduction

Shellac, the lac resin secreted by the insect *Laccifer lacca* Kerr, when subjected to alkaline hydrolysis, affords a number of hydroxyaliphatic and sesquiterpenic acids[1]. Aleuritic acid (9, 10, 16 - trihydroxypalmitic acid) is the major aliphatic acid and is present to an extent of 32-35%[2,3]. The structural features of this acid, *viz.*, vicinal hydroxyls with threo configuration and the presence of terminal hydroxyl and carboxyl functional groups, render it an excellent starting material for the synthesis of several perfumery chemicals like macrocyclic lactones and ketones and various bioactive compounds like prostaglandins and pheromones[4]. Its isolation from seed lac by alkaline hydrolysis is reported to yield a technical grade material in *ca* 25 % yield[5,6]. Often this material requires to be reprocessed to the desired level of purity. The lac pigments may be decolourized by pretreatment of the resin with a hypochlorite solution. But this does not improve the purity of the end-product. Also, the other problems encountered in the production of aleuritic acid include the prolonged saponification (over 10 days), the slow rate of filtration and the gradual reduction of yields while reprocessing the acid to obtain a purer product. A systematic evaluation of the process was therefore undertaken with a view to achieving standardization of the isolation procedure and getting a quality product in optimum yield.

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Materials

Commercial seed lac was used in the experiments. Sodium hydroxide flakes used were of `Rayon grade' and other chemicals were of LR grade. Solvents used were of analytical quality.

Method

Isolation of aleuritic acid from seed lac, typical procedure: Sodium carbonate (75 g) was dissolved in water (1.2 l) and the solution heated to 90-95°C. Seed lac (300 g) was dissolved in it by adding in small portions while stirring the mixture. The stirring was continued until the solute completely dissolved (3 h). The mixture was allowed to remain at 90-95° C for 3 h without stirring and then cooled to 25° C. Crude wax floating on the surface was skimmed off and the solution filtered through a mull cloth to remove the remaining insoluble material. Wax and the solid residues added upto 24 g. Sodium hydroxide flakes (120 g) were added in small amounts to the filtrate under stirring over a period of 30 min. Then sodium sulphite (60 g) was added to the solution followed by Sodium chloride to saturation (192 g, 16% w/v). The resultant thick, purple coloured solution was allowed to stand at room temperature and repeatedly filtered through 'Terrycot' cloth at regular intervals (24 h.) until no more precipitate separated out from the filtrate. The combined precipitates were redissolved in 300 ml hot water (70-80° C) and filtered hot under suction through a filter paper to collect a red pigment (5-10 g). The filtrate was cooled to 10°C and allowed to stand for 2 h. Sodium aleuritate

Table 1 -Processing of seed lac* to yield aleuritic acid

Entry No	Water ml	NaOH gm	NaOH %W/V	Na_2SO_3 gm	NaOCl ml	Sapon. Time (Days)	Yield gm	Yield %
1	1450	290	20	—	—	10	53	17.6
2	1350	270	20	60	—	10	60	20.0
3	1250	250	20	60	—	5	57	19.0
4	1200	240	20	—	—	5	59	19.6
5	1200	240	20	60	—	5	64	21.3
6	1200	60	5	60	—	5	30	10.0
7	1600	160	10	60	300	5	65	21.6
8	1200	120	10	60	300	5	61	20.3
9	1200	240	20	60	300	5	68	22.6
10	1200	120	10	60	—	5	70	23.3

*300 g of seed lac was processed in each experiment.

separated out as fine micro crystalline solid which was filtered under coarse vacuum (25-30 Torr). It was redissolved in 300 ml of hot water, the solution cooled and acidified to pH 3 using chilled 3N sulphuric acid. The separated solid was filtered at the pump and dried in an open pan at ambient temperature in a current of air. Aleuritic acid thus obtained was a creamy white solid. The process is summarized in flow chart (Fig.1) and the yields of aleuritic acid obtained in different experiments are presented in Table 1.

Purity Assay of Aleuritic Acid

Derivatization of the Acid

Diazomethane (16.6 mmol) was generated by the action of ethanolic potassium hydroxide (5 g KOH in 8 ml water and 10 ml ethanol) on N-methyl-N-nitroso-*p*-toluenesulphonamide (5 g, *Diazald*, Aldrich) in ether(45 ml) and distilled along with ether in a special apparatus[7]. The ethereal solution of diazomethane (40 ml) was slowly added in cold to a methanolic solution of aleuritic acid (5 g in 30 ml) and the mixture allowed to stand for 30 min at ambient temperature. The solvents were distilled off to get a solid (5.20 g) which was treated with acetic anhydride (5 ml) and pyridine (5 ml) at 50°C on a water bath for 1h. The mixture was poured onto crushed ice and the gummy solid that separated was extracted with ether. The ethereal solution was successively washed with 1N HCl, saturated $NaHCO_3$ and water, dried over anhydrous Na_2SO_4. Distillation of the solvent gave a low-melting solid (7.20 g) that was characterized as triacetyl derivative of methyl aleuritate by ^1H NMR (90 MHz, CCl_4 ppm): 4.93(m.2H), 4.00(t,2H,J = 6Hz), 3.60(s,3H), 2.26(t,2H,J = 6Hz), 2.03(s,6H), 2.00(s,3H), 1.10-1.63(m,22H).

GC Analysis

The aleuritic acid derivative (100mg) was dissolved in 2 ml acetone and 1 µl of the solution was injected into a HP 5730 Gas Chromatograph fitted with H_2 FID under the following conditions: Carrier gas: N_2, 30ml/min. Column: OV - 101, 10% on Chromosorb W, SS Column, 6' X 1/8" O.D. Temperature progr.:200 /8 per min./ 300 ° C. Detector temp.: 300°C, Inj. temp.: 250 °C. Purity of the acid was determined by relative area percentages of the peaks.

Results and Discussion

The effect of several parameters on the yield of isolated aleuritic acid from seed lac can now be understood from the results of the various experiments conducted in the present study (Table 1). The optimum ratio of seed lac to water is 1:4 (w/v). This was arrived at by determining the minimum amount of water required to dissolve the reactants. Higher quantitiy of water is undesirable for two reasons. Firstly, a certain amount of sodium aleuritate is always retained in the filtrate and secondly, more alkali would be needed for the saponification on w/v basis. Use of sodium sulphite definitely increased the yield. Monitoring of the reaction showed, that under the optimised conditions, saponification of the resin was complete in five days. Thus, under these conditions, aleuritic acid of + 92 % purity was obtained in 23.3 % yield (entry 10, Table 1). Purity of the acid was determined to be 92 % by the GC analysis of its tri-O-acetyl methyl ester derivative. This procedure is an alternative to the one reported earlier for the analysis of the alkaline hydrolysis products of shellac[8]. The use of sodium hypochlorite in the process yielded a bright white product of comparable purity. While this process required more alkali for saponification (entry 9), it had no obvious advantage over the former.

Notable alterations effected in the process are indicated in the flow chart. Earlier workers[3,5] set about direct dissolution of the crude sodium aleuritate in hot water followed by cooling and

FLOW CHART

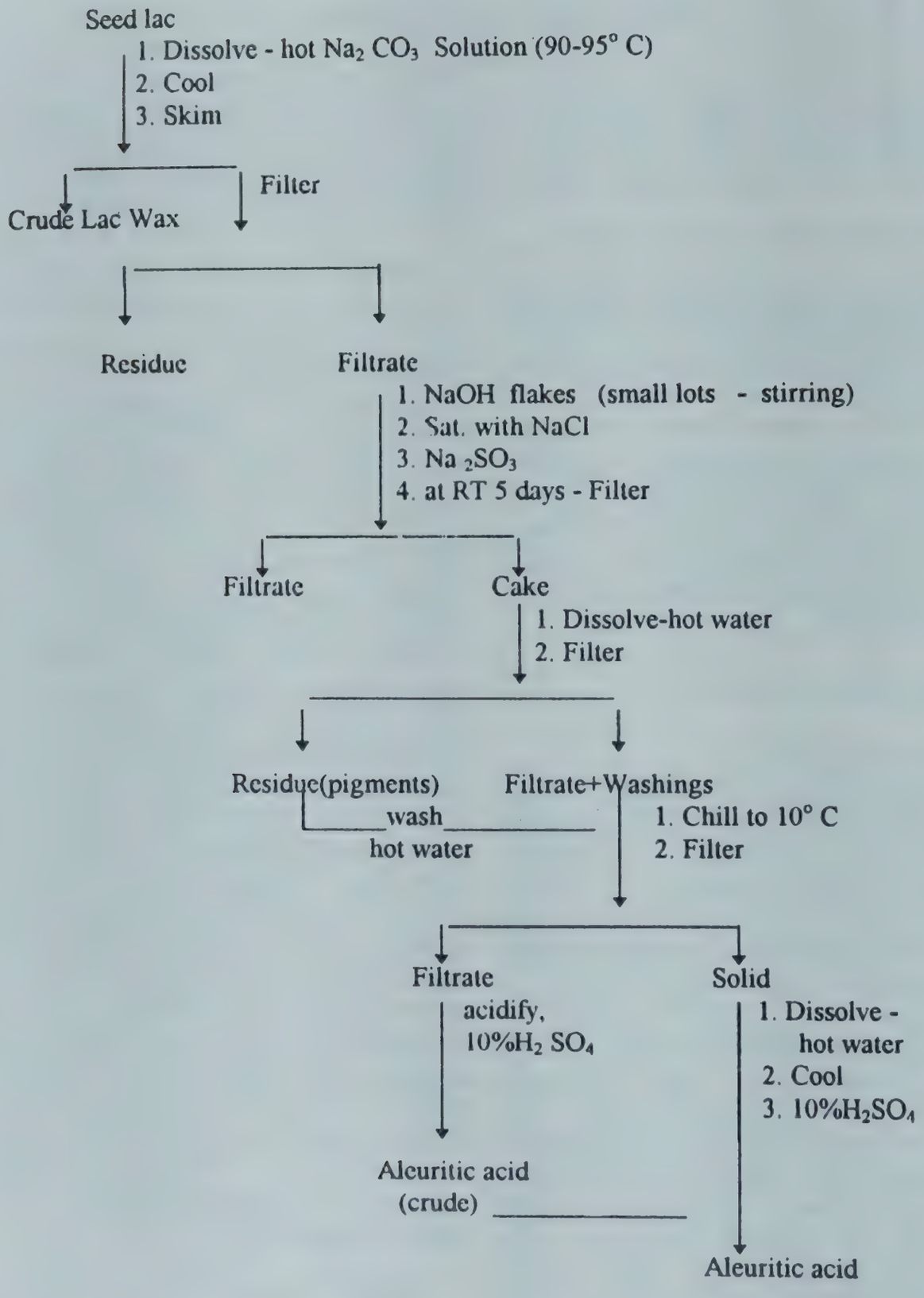

Fig. 1—Flow Chart of the process of manufacture of aleuritic acid from seed lac

acidification with dilute acid. Such a product would have nonvolatile impurities which may persist in the perfumery chemicals derived from it and affect their quality. Purification of the acid by crystallisation is not only laborious but also unattractive from the point of yield. In the present process, a simple step of crystallisation of the crude sodium aleuritate from water has been introduced which effectively removes gummy pigments and other nonvolatiles. This step also obviates washing of the salt with saturated brine solution which, is not only a tedious and time consuming process, but also leads to loss of solids. Other significant features of this process are the optimization of the quantity of water and the base used for saponification and substantial reduction in the reaction time.

This new improved laboratory process for the preparation of aleuritic acid from seed lac is amenable for exploitation on a commercial scale.

Acknowledgements

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References

1. Bose P K , Sankaranarayana Y & Sengupta S C, *Chemistry of lac* (Indian Lac Research Institute, Ranchi), (1963).
2. Khurana R G, Singh A N, Upadhya A B, Mhaskar V V & Sukh Dev, *Tetrahedron* **26** (1970) 4167.
3. Singh A N, Upadhya A B, Mhaskar V V & Sukh Dev, *Tetrahedron* **30** (1974) 867.
4. Subramanian G B V & Bhushan K H, *Perfumer & Flavorist* **18** (1993) 41.
5. Agarwal S C, Srivastava B C & Majee R N, *Res. Ind* **33** (1988) 243.
6. Prasad N & Agarwal S C, *Res Ind* **35** (1990) 164.
7. DeBoer T J & Backer H J, *Organic synthesis Coll.*, (Wiley, NewYork) Vol IV, (1963) 250.
8. Chauhan V S, Sriram N & Subramanian G B V, *J.Chromatography* **84** (1973) 51.

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Kinetic Approach to Interpret the Delignification of Egyptian Bagasse Organosolv Pulping Process

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Pulping of egyptian bagasse was carried out in 50 per cent aqueous butanol in absence and presence of 12 per cent NaOH to determine the delignification rates respectively. The kinetic behaviour of the delignification of bagasse organosolv process was studied within fixed temperature and time ranges. In the absence of alkali, the delignification rate of aqueous butanol pulping kinetically was found to behave as first-order reaction with activation energy of 35.44 Kcal.mol^{-1}. However, in presence of alkali, the delignification rate of alkali butanol pulping has overall second-order reaction with activation energy of 61.88 Kcal.mol^{-1}. The numerical variation of the two computed activation energies from those published in literature is attributed to the encounter frequencies and solution effect.

Introduction

Delignification rate of lignocellulosic materials by using organosolv process was affected by several independent variables namely solvent concentration, time and temperature of pulping process and type of lignocellulosic material [1-3]. Generally, during the pulping process, the effect of pure butanol alcohol relative to the aqueous-butanol in delignifying the lignocellulosic materials is negligible.[4]

Addition of water to pure butanol accelerates the bagasse pulping-process until critical ratio is reached. Above this ratio, the degradation of carbohydrate(s) is enhanced rather than the delignification occurring[5]. The optimum water-butanol ratio was experimentally determined as 50 per cent[4]. Addition of 12 per cent NaOH above the ratio increases the delignification rate with higher yield [6-7]. The kinetic behaviour of organosolv delignification process was found similar to Kraft pulping process [8-9].

In this paper, the kinetic behaviour of delignification of egyptian bagasse with butanol-water organosolv pulping process in absence and presence of 12 per cent NaOH at different pulping temperatures within fixed time intervals is reported.

Experimental Procedure

Bagasse is the raw lignocellulosic material and was provided by the Edfo-Mill, Egypt. This egyptian bagasse was cooked with 50 per cent water-butanol ratio in absence and presence of 12 per cent NaOH.The pulping process was made to proceed in a stainless steel cup of 2 l capacity rotating in ethyleneglycol bath and provided with built-in electrical heating. The measurements were taken within a fixed temperature range (160-190°) with intervals of 10° C for a fixed period of 3 hr at intervals of 0.5 hr. Lignin determination was carried out as per Tappi standard method T222 05 - 54.

Results and Discussion

Kinetic behaviour of egyptian bagasse delignification in 50 per cent aqueous butanol system

In absence of alkali 12 per cent NaOH

Figure 1 indicates for each pulping temperature, a rapid decrease in the percentage of the residual lignin at the early beginning of pulping process. The amount of decreasing lignin is directly proportional to the pulping temperature. However, by introducing gradual increase in the time of pulping process, the decreasing rate of the residual lignin in the produced pulping was found to vanish gently. The above behaviour could be attributed to the increase in the

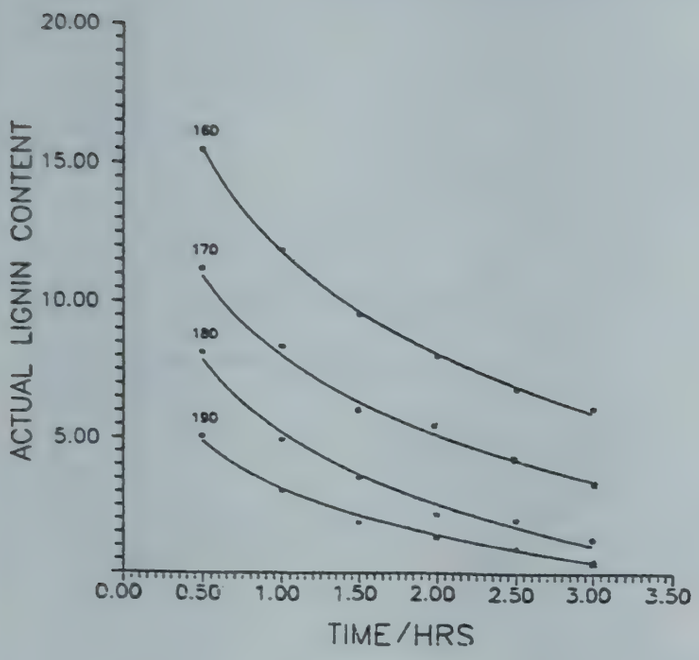
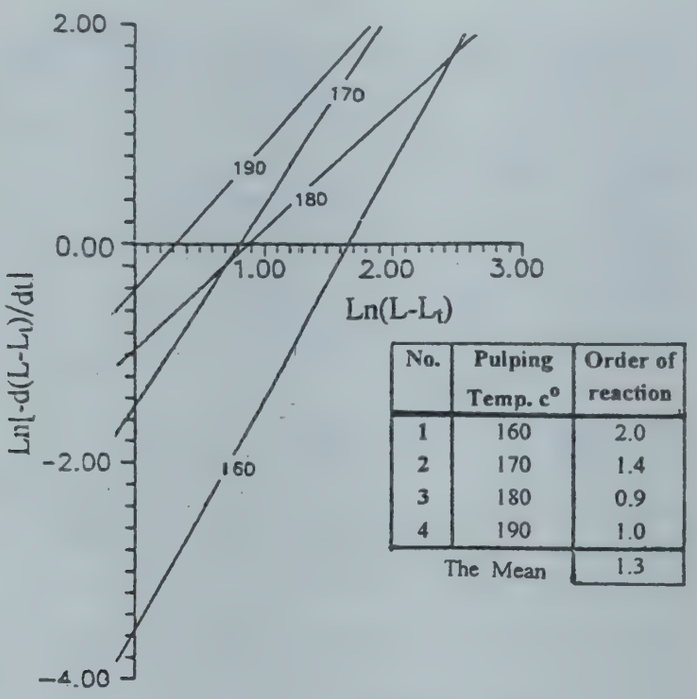


Fig.1—Kinetic behaviour of delignification of bagasse in aqueous butanol at different temperatures with a fixed pulping period.



No.	Pulping Temp. c°	Order of reaction
1	160	2.0
2	170	1.4
3	180	0.9
4	190	1.0
	The Mean	1.3

Fig.2—Graphical determination for the rate and order of delignification process of bagasse in aqueous-butanol medium.

miscibility of butanol in-water due to increase in the temperature. As a result, the penetration rate of pulping liquor through the bagaqsse raw materials enhances the delignification rate [10-11].

Based on the degradation behaviour of the delignifying curves of Fig.1, the delignification rate could be represented by the following consecutive irreversible reactions model:

$$L \xrightarrow{k1} aDL+ \begin{cases} \xrightarrow{k2} bDL \\ \xrightarrow{k3} cPL \end{cases} \qquad ...(1)$$

where a > b + c

It is believed that in the aqueous medium the etheronic bonds of the lignin macromolecule L could be cleavaged to produce a number of reactive degraded fragments , aDL+.

By neutralization process via nucleophilic species, which might exist in the reaction pulping liquor, soluble lignin bDL could be formed. It is also believed that, simultaneously, the recondensation reaction between the reactive degraded fragments, produces insoluble lignin polymers (cPL).

It is clear that the major part of the delignification process mainly depends on the formation of the reactive intermediate DL+ fragments. At the very beginning of the pulping process, the concentration of DL+ fragments builds up from zero, and at the end of the delignification process drops again to be zero. So, it can be concluded that the concentration of DL+ is usually smaller than the concentration of L by a factor at k1/k2 or k1/k3 based on the neutralization or recondensation processes respectively. Therefore,

$$[DL+]^b = (k1/k2)L \qquad ...(2)$$

and

$$[DL+]^c = (k1/k3)L \qquad ...(3)$$

thus

$$[DL+]^{b-c} = (k3/k2) \qquad ...(4)$$

From the consecutive reaction equations we have

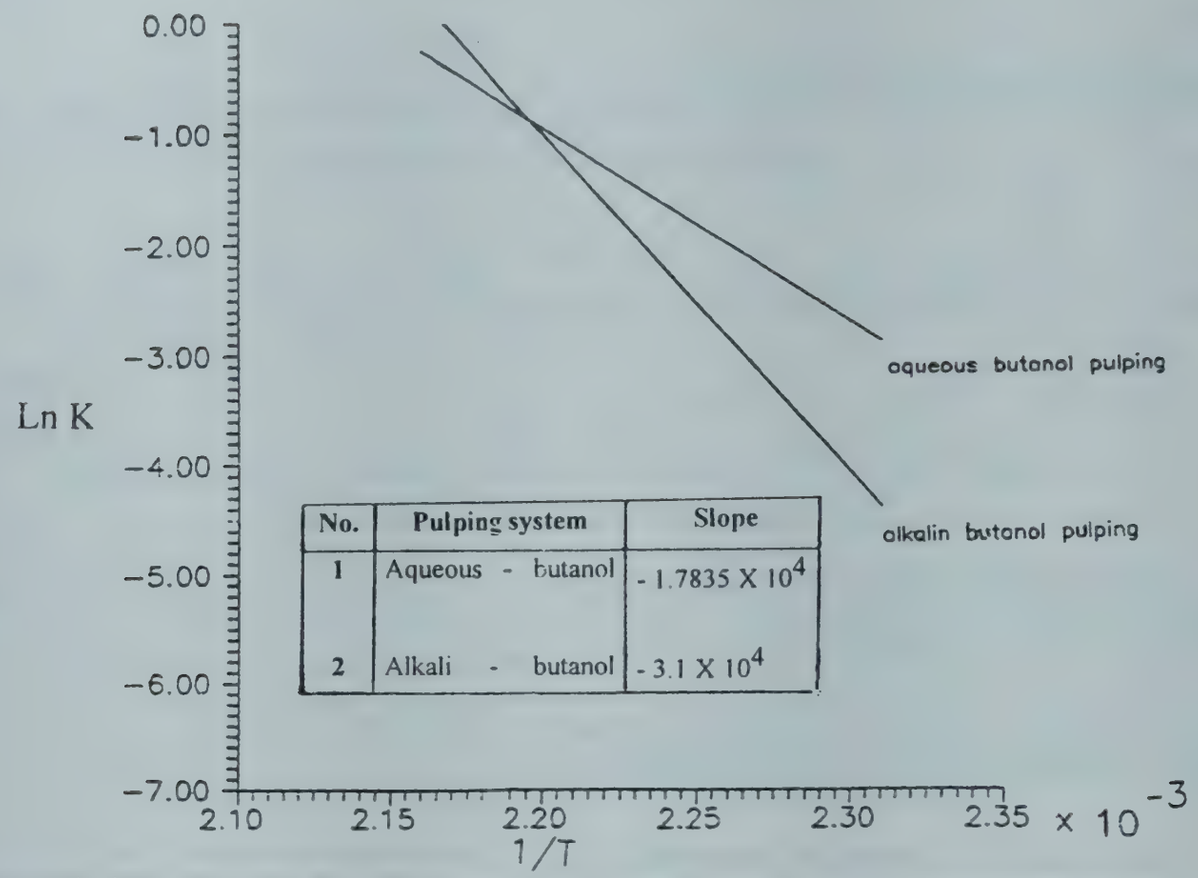
$$k1[L] = k2[DL+]^b + k3[DL+]^c \quad ... \quad (5)$$

rate of degrading the the macro lignin molecule — rate of forming soluble lignin — rate of forming polymer lignin

considering a = b + c and multiplying both sides of Eq.(5) by $[DL+]^b$ and then dividing by $k2[DL+]^{2b}$, we have,

$$(k1/k2)[L][DL+]^{-b} = 1 + (k3/k2)[DL+]^{a-2b} \quad ... \quad (6)$$

Substituting Eqs.(2) and (4) in Eq.(6)



No.	Pulping system	Slope
1	Aqueous - butanol	-1.7835×10^4
2	Alkali - butanol	-3.1×10^4

Fig3—Arrhenius type behaviour plots of aqueous and alkaline butanol bagasse delignification pulping process.

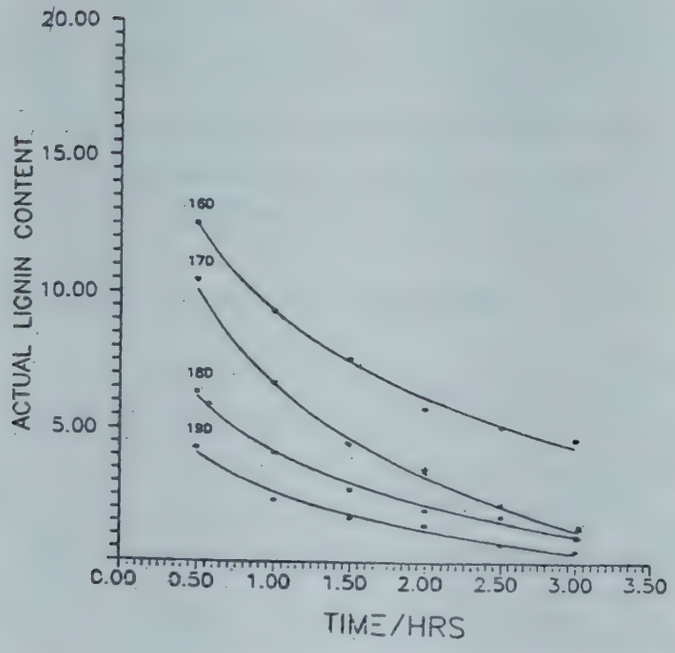


Fig.4—Kinetic behaviour of delignification of bagasse in alkali-butanol at different temperatures within a fixed pulpling period.

$$[DL+]^0 = 1 + [DL+] \quad ...(7)$$

Therefore,

$$[DL+] = 0$$

and finally,

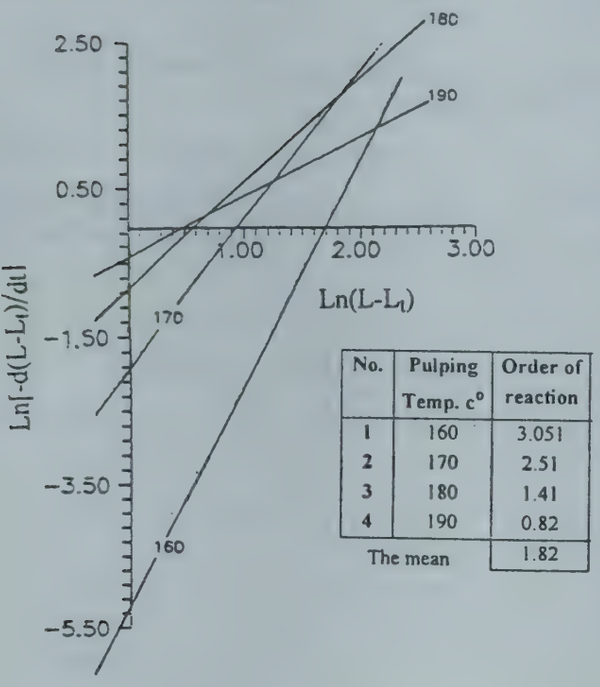
$$d[DL+]/dt = 0$$ at any time of reaction

Therefore the bagasse pulping in aqueous butanol must be allowed to proceed as first order.

Figure 2 indicates the relation between Ln[-d(L-L_t] and residual lignin, Ln(L-L_t) for each pulping temperature at each time interval. The intercepts of the straight lines with Ln[-d(L-L_t] axis indicate that the rate constant of aqueous butanol delignification process increases by increasing the temperature. While the overall reaction order which was calculated as the mean value of the slopes ;of the plotted lines was found to be 1.32 ~ 1.0 (i.e. it could be considered as a first-order reaction).

The exact agreement between the experimental results and the proposed kinetic model indicates that the steady-state approximation can be applied, since the delignification process mainly depends on the reactive intermediates at constant concentration. So, one can deduce that d[DL+]/dt determines the reaction.

Figure 3 shows the relation between Ln k(s) of the straight lines of different pulping temperatures and the reciprocal of these pulping temperatures. Using the slope of the plotted straight line, which shows Arrhenius-type behaviour, the activation energy of the aqueous-butanol egyptian bagasse pulping delig-



No.	Pulping Temp. c°	Order of reaction
1	160	3.051
2	170	2.51
3	180	1.41
4	190	0.82
The mean		1.82

Fig.5—Graphical determination for the rate and order of delignification of bagasse in alkali-butanol medium.

nification process was calculated as 35.44 Kcal. mol^{-1}.

In presence of alkali 12 percent NaOH

Figure 4 exhibits the kinetic behaviour of bagasse delignification process at each pulping temperature over all pulping period. The presence of alkali in aqueous butanol pulping liquor accelerates the rate of delignfication due to direct reaction with the reactive degraded lignin fragments to produce much soluble product(s)[12-13]. Therefore the recondensation chance of the residula lignin fragments on cellulosic fibres is decreased. This is a simple explanation to interpret the observed improvement of the delignification rate of bagasse pulping process with time and temperature in the presence of alkali than in its absence (cf Fig.1). This behaviour indicates that NaOH accelerates the delignification rate by enhancing the hydrolysis rate of benzyl ether links to form stable benzyl carbonium ions[14-15].

Figure 5 shows the straight line relations between Ln[-d(L-L_t/dt] and Ln(L-L_t) for each pulping temperature. The rate constants of alkali-butanol pulping process at each pulping temperature are determined via the intercepts with the Ln[-d(L-L_t)dt] axis. Also the order of the alkalin delignification process was calculated as the mean value of the measured slopes of the plotted straight lines of different pulping temperatures. The calculated mean value is 1.8 ~ 2.0. Thus it could be considered as a second-order reaction. This result confirmed that the alkali-butanol delignification process of bagasse pulping is directly affected by the NaOH concentration. By applying Arrhenious equation, the activation energy of this second-order reaction was computed as 61.6 Kcal.mol^{-1} (cf Fig.3).

The role of sodium hydroxide in the delignification process could be described in the following mechanism. Sodium hydroxide, during the pulping process functions in a dual role defined as converting the lignin to its more soluble sodium derivative(s) and removing the low-molecular weight carbohydrate components from the cell wall structure. These double functions of NaOH cause a dilatation of pores in the raw material and an increase of the accessibility of pulping liquor inside the ligno-cellulosic matrix.

The above pulping mechanism could be expressed in the following reaction mode:

$$[L] + [NaOH] \underset{k-2}{\overset{k1}{\rightleftharpoons}} [LNa] \xrightarrow{k2} [DL] \quad \ldots (8)$$

Conc. of macro molecules of the raw material	Conc. of alkali in liquor system	Soluble LNa derivatives	Soluble lignin in alkali liquor

The above speculated reaction is a consecutive reaction in which the intermediate attains an equilibrium with the reactants. This is called pre-equilibirum. Therefore,

$$d[LNa]/dt = k1[L][NaOH] - k\text{-}2[LNa] \quad \ldots(9)$$

If the steady state approximation rules are applied

$$k1[L][NaOH] = k\text{-}2[LNa] \quad \ldots(10)$$

$$[LNa] = k1/k\text{-}2[L][NaOH]$$

So k1/k-2 could be termed as equilibrium constant K.

$$[LNa] = K[L][NaOH] \quad \ldots(11)$$

The formation rate of the soluble lignin product [DL] then is given by

$$d[DL]/dt = k2K[L][NaOH] \quad \ldots (12)$$

Therefore, the delignification reaction of the alkali-butanol organosolv pulping has over all second-order kinetics, since the concentration of NaOH acting in Eq.(12) represents the rate of soluble lignin formation.

References

1. Atchison J E, *Tappi Pulp Conf Proc,* **7**(1979)
2. Azia S & Lora J, *Tappi J*, **68**(8)(1985)49.
3. Sarkanen K V, *Holzforsch*, **43**(1989)239.
4. Bailey J H, *Ind Eng Chem*, **36**(1942)651.
5. Dahlman G & Schroeter M C, *Solvent Pulping Conf Proc,* Integrated Paper Service Inc, 1980, p.7
6. Atsushi K, Azuoma J & Koshijina T, *Holzforsch,* **38** (1984) 141.
7. Peng F & Smonson R, *Appita* **42** (1989) 458.
8. Thomas J Me D, *Tappi*, **76**(8) (1993) 92.
9. Parki J K & Phillips J A, *Chem Eng Commun,* **65** (1988) 187.
10. Nada A M A, Fahmy Y & Abou-Yousef H E, *J Sci Ind Res,* **55** (1996) 516.
11. Arnovsky S I & Gortner R A, *Ind Eng Chem,* **22** (1940) 264.
12. Kleinert T N & Tayenth K V, *Ztsch Angew Chem,* **44** (39) (1981) 788.
13. Lora J H & Wayman M, *Tappi*, **61**(6) (1978) 55.
14. Roh J K & Shin D S, *Tappi*, **68**(2) (1985) 50.
15. Ghose T K, Pannir P V & Ghose P, *Biotechnol Bioeng*, **25** (1983) 2577.

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Alkaline Roasting as a Route for Extraction of Potassium from Feldspar

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The extraction of potassium from feldspar (orthoclase) using the roasting route is studied. The process involves roasting of feldspar with different fluxes individually or in combination followed by leaching of the roasted mass under reflux with water. The use of different fluxes such as sodium carbonate, calcium carbonate, calcium sulphate, magnesium sulphate and sulphate, chloride and nitrate of ammonia is studied. The study also includes roasting of feldspar with rare earth salts. Flame photometric analysis indicates potassium extraction of the order of 80% with sodium carbonate or a mixture of calcium carbonate and calcium sulphate.

Introduction

Potassium is a strategic element signified by its use in agriculture as well as defence, both of which contribute to the progress of a country. India is a country with vast agricultural base and as such ranks high among the fertilizer consuming countries of the world. But, the country's entire requirement of potassium for fertilizer industries (about 1.5 lakh tonnes per annum)[1] is met through imports, as indigenous deposits of soluble potassium salt are not available. However, there are vast deposits of feldspar in Madhya Pradesh, Rajasthan and Andhra Pradesh containing considerable amounts of potassium awaiting exploration. Feldspar, generally composed of the silicates of aluminium and potassium, forms 60% of the world's igneous rocks but is considered only as a secondary source of potassium. It may be of interest to note that the need for processing feldspar was felt during the first quarter of this century when several studies carried out on feldspars resulted in innumerable patents. However, Indian feldspars were not the subject of any such study. The authors have therefore taken up this investigation. In an earlier communication[2] the authors have reported the extraction of potassium from feldspar by acid leaching or fusion with selected fluxes. In the present study the authors have presented the extraction of potassium from feldspar by roasting with different fluxes individually or in mixtures and then leaching with water.

Materials and Method

All the reagents were of analytical grade. The feldspar sample from Rajasthan had the following composition: SiO_2, 64%; Al_2O_3, 19%; Fe_2O_3, 0.13%; CaO, 0.8%; Na_2O, 2.25%; and K_2O, 13%. The sample was ground to −400 mesh before use. A digital flame photometer of Indian make (Systronix) was used for flame photometric studies. A muffle furnace with 10°C accuracy was used for roasting.

The roasting experiments were carried out using (i) individual fluxes which were either alkali or alkaline earth salts, (ii) mixture of these fluxes, and (iii) rare earth salts.

(i) Roasting with Individual Fluxes

The samples (each 10g) of feldspar (−400 mesh) were mixed thoroughly with alkali or alkaline earth salts in required proportions, transferred to porcelain crucibles and heated at the desired temperature for 4-5h.

The roasted mass was cooled, mixed with water and refluxed with stirring for 5-6h. The leach solutions were analysed for potassium by flame photometry. The results are presented in Table 1.

(ii) Roasting with Flux Mixtures

The above procedure was followed here also, replacing the individual fluxes with mixtures of fluxes. The results are given in Table 2.

Table 1 — Potassium extraction by roasting feldspar with fluxes

Sl No.	Flux	Flux-feldspar ratio	Temp, °C	Recovery, %
1	$CaCO_3$	5:1	900	12
2	Na_2CO_3	5:1	900	80
3	$(NH_4)_2SO_4$	7:1	425	17

Table 2 — Potassium extraction by roasting feldspar with mixture of fluxes

Sl No.	Flux mixture	Flux-feldspar ratio	Temp, °C	Recovery %
1	$CaSO_4$ & $CaCO_3$	0.75:3:1	900	79
2	$CaSO_4$ & $MgCO_3$	0.75:3:1	900	18
3	$MgSO_4$ & $CaCO_3$	0.75:3:1	900	60
4	$(NH_4)_2SO_4$ & NH_4Cl	1:1:1	425	4
5	$(NH_4)_2SO_4$ & NH_4NO_3	1:1:1	425	5
6	NH_4Cl & NH_4NO_3	1:1:1	425	4
7	Li_2CO_3 & Na_2CO_3	2.5:2.5:1	600	50

Table 3 — Potassium extraction by roasting feldspar with rare earth salts

Sl No.	Rare earth salt	Flux-feldspar ratio	Temp, °C	Recovery %
1	Cerium oxide	5:1	900	2.0
2	Neodymium chloride	5:1	900	2.0
3	Samarium carbonate	5:1	900	2.0
4	Yttrium oxide	5:1	900	1.5
5	Cerium oxalate	5:1	900	2.5

(iii) Roasting with Rare Earths

These roasting experiments were carried out replacing the fluxes with rare earth salts. The potassium recoveries are shown in Table 3.

Results and Discussion

The amounts of potassium recovered after roasting feldspar with a few representative fluxes are given in Table 1. These fluxes and their quantities were chosen after considering several factors which included the cost and ready availability of these fluxes, resulting by-products, leaching properties of the roasted mass and literature survey. All the fluxes yielded considerable amount of water-extractable potassium, indicating their efficacy in disintegrating the matrix. Alkali carbonates have been found to be more effective with sodium, bringing 80% of the available potassium into solution. This is possible because Na^+ is isomorphically exchangeable with K^+ in the silicate lattice and is therefore highly effective in driving K^+ from the aluminosilicate network[3]. This could also be attributed to the well known fusion effect of sodium carbonate. The fusion temperature of 900°C was brought down to ~600°C by adding lithium carbonate but with less recovery of potassium (Table 2). The lower recoveries with ammonium sulphate may also be attributed to the low temperature of heating; however at temperatures > 425°C the salt evaporates. It is interesting that roasting with calcium carbonate resulted in much less recovery.

The system may be better understood if a combination of fluxes is used. Table 2 represents the data on these studies. It is clearly seen from these results that the inclusion of an oxidizing ion in the flux did not help in sizeable recoveries of potassium if the roasting temperature is low, as with the combination of ammonium salts (Sl Nos. 4, 5 and 6). Addition of calcium sulphate to the calcium carbonate resulted in a remarkable increase in potassium recovery to the extent of 79% conforming to the assumption that the reaction mechanism involved decomposition of calcium carbonate followed by the formation of calcium silicate[4]; this enables the released potassium and aluminium to react with calcium sulphate to form water-extractable sulphates. Obtaining of similar results when magnesium sulphate was replaced with calcium sulphate (Sl No.3) supports the mechanism. The yields were relatively lower (60%) obviously due to the comparatively higher stability of magnesium sulphate. when magnesium carbonate and calcium sulphate were used as fluxes (Sl No.2), the yield was very low. This was on expected lines as magnesium carbonate is known to undergo complete de-

composition before 600°C and the MgO thus formed was not effective in opening the feldspar matrix[5]. The results suggest further detailed investigations.

It is interesting that quite a few metal salts were investigated for the decomposition of feldspar but rare earth salts somehow escaped the attention of researchers. As rare earths have a tendency to react with double salts to form a stable perovskite structure[6], relatively smaller amounts are required to effect the release of potassium from feldspar. Extremely poor recoveries, as evident from Table 3, however, indicate that rare earths are quite ineffective for the purpose under the conditions of study. Nevertheless, further experiments under varying conditions are needed before ruling out their impact.

Conclusions

(1) Potassium can be obtained in soluble form from Indian feldspars by roasting with either sodium carbonate or a mixture of calcium carbonate and calcium sulphate.

(2) The temperature of decomposition of fluxes as well as of the roasting is important to effect the opening of feldspar matrix.

(3) Rare earth salts when added in 1:5 proportion to feldspar and roasted at 900°C are not at all effective in bringing out potassium in water-extractable form.

Acknowledgement

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References

1 Soni M K, *Mining Eng*, **7** (1990) 3.

2 Nayak R, Suryanarayana A, Rao J R, Rao S B & Nayak B B, Indian Mineral Industry — Energy Environment and Resource Development (Allied Publishers Limited, New Delhi), 1995.

3 Rao B R, Rao L S, Mazumdar A K & Rao T C, *Mineral Eng*, 6(4)(1993) 405.

4 Saxena E R & Datar D S, *J Indian Chem Soc, Ind & News Ed*, **14** (1951) 36.

5 Kirpatrick F A, *Trans Am Ceram Soc*, **18** (1916) 575.

6 Rao J R, Nayak R, Parida K M, Thakur R S, Das S N & Rao S B, *Asian J Chem Rev*, **2** (1991) 126.

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BOOK REVIEWS

State of the Art in Polymer Science and Engineering in India, by Professor M Santappa (T R Publications Pvt Ltd, Madras 600 017) 1996, pp 576 +xii, Price: Rs 795.00
[ISBN 81 85427 52 6]

The book under review is an interesting compilation of the published work conducted in Indian institutions in the area of polymer science and engineering. The author of the compilation is a preeminent Indian scientist, who pioneered polymer research in India in the early fifties at the A C College of Technology, University of Madras.

The book is divided into eight sections, namely (i) synthesis of novel monomers, catalysts and polymers (63 pages, 376 references), (ii) kinetics of polymerization (43 pages, 1090 references), (iii) graft copolymerization (35 pages, 462 references), (iv) physical chemistry of polymers (46 pages, 965 references), (v) chemical engineering and technology of polymers (85 pages, 331 references), (vi) some properties and uses of polymers (85 pages, 601 references), and (vii) application of polymers in industries (51 pages, 113 references). Section 8, divided in two parts, is devoted exclusively to science and technology of leather with extensive bibliographic coverage of work done by Indian scientific establishments in this area.

Each section deals with the work in that area, organized institution-wise. The research activities of the scientists are described in a narrative style. Each section ends with conclusion and recommendations, wherein, the authors attempts to evaluate the impact of the work in India and defines its future directions. The literature coverage in each section is up to 1992.

The author should be complimented for successfully undertaking a work of this magnitude. It is an excellent compilation of bibliography of Indian research efforts in the area of polymer science and engineering. It reflects the geographical spread of institutions involved in research in this area and their relative emphasis.

The book also raises some serious questions about the quality and relevance of research in polymer science and engineering in India. Although the author has steered clear of any critical views on the subject, his thoughts are apparent in a reading of the Preface. He says "much of the work published is repetitive, uninteresting and not very useful from the fundamental or applied aspects". It will be useful for everyone involved in this area to introspect deeply and understand what lies at the root of this malaise.

The book is also mirror as to where we stand today in this significant area of science and technology. In the historical past, the physical chemists naturally gravitated to this field and this is evidenced by over two thousand publications from Indian scientists in the area of kinetics of polymerization and physical chemistry of polymers. Unfortunately, the vast body of organic chemists in this country still tend to look upon the science of macromolecules with some skepticism. Hence, in India, pitifully poor attention is being paid to the synthesis of polymers. Worldover, polymer synthesis is today experiencing a rebirth — thanks to the armory of reagents and catalysts that have become known to chemists in the recent years for chemo-regio and enantioselective carbon-carbon bond formation. Similarly, practically no research is conducted in India in the experimentally more demanding and scientifically challenging areas of anionic, cationic, ring opening metathesis and Ziegler Natta polymerizations. Even some of the more dramatic developments in the area of free radical polymerizations have eluded our grasp in spite of our long history of research in this field [*see*, Sivaram S, *J Sci Ind Res*, 56 (1) (1997) pp 1-16]. The contribution of the polymer industry to research in this area is dismal. Only one company, namely, Indian Petrochemical Corporation Limited, finds a place in the book. The Indian polymer scientists should also ask themselves, why in spite of such a large number of published research, the impact of this science on industry, in terms of new processes and products, has been so poor.

In summary, the book will be a useful addition to the library of every institution, involved in research in polymer science and engineering. It will also be a useful volume to those agencies administering science in India in terms of both policy and research funding.

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The ecological wisdom of nature Inc.

Steering Business Toward Sustainability, edited by Fritjof Capra and Gunter Pauli (Sage Publications, New Delhi 110 048) 1996, pp 191, Price: Rs 195/= (paper)
[ISBN 81 7036 572 4]

In the post-Cold War era, one of the most pressing concerns that has preoccupied planners, economists, scientists, and the increasingly visible community of NGOs, is the degradation of the environment to the extent that the stability of the ecosystem on a planetary scale is threatened. It appears that today the bull has to be taken by the horns, and that this threat cannot go away by simply appealing to a gigantic population smitten by the consumerist bug to alter its life style, or pleading with governments to implement stronger regulations to control pollution or arrest the march to ecological doom. At one level, the current emphasis accorded to sustainability by development agencies, reflects the sense of urgency underlying core ecological concerns, and at another reflects the need to set up a distance from the older, model of development, that preoccupied planners and policy makers of the 1950s and 1960s.

Other than departing from the axiomatics of the earlier frame of development, the notion of sustainable development circumvents, what formerly was visualized in terms of, the dichotomy between developmental concerns and environmental issues. Sustainable development seeks to integrate the concern for the environment with the developmental imperative, albeit a different kind of development. The latter requires the transformation of industrial practices in order to ensure sustainable development in global terms. The book under review exemplifies the attempt to take the new paradigm (which has been discussed in Capra's earlier books) into the industrial sphere, that has thus far been driven by the desire to augment profits, expand scales of production, and capture as much of the market share as possible—this rapacity has been partially responsible for the present crisis. The book therefore brings together the devil and the good lord in an effort to proselytize the devil, to inform industry that there will be no more profits for them if they did not redefine their practices and culture on the model of sustainability. As a collection of essays, this volume not merely accentuates the dimensions of the problem, but illustrates how the transformation of industrial practices and culture may be undertaken through a couple of case studies of profit making industrial houses who have reinvented their companies in eco-friendly terms.

The introductory chapter by the editors of the volume sets the tone and outlines the dimensions of the challenge, by placing the onus for ecological restoration on business houses, for it is they who have to create 'sustainable forms of business, embedded in sustainable communities'. But how does business remodel itself so that it can take on this major challenge posed for it by the times. Drawing inspiration from a 'deep ecology' perspective, and their model from the theory of living systems, the authors identify eight core principles of ecology: interdependence, ecological cycles, energy flow, partnership, flexibility, diversity, co-evolution, and sustainability. These principles of ecology are then extrapolated beyond the conventional boundaries of their applicability in order to reorganize business practices. This exercise it is hoped would get to the root of the tension between economics (dealing with quantity, expansion and competition) and ecology, so that a new economic paradigm dealing with quality, cooperation, and conservation will emerge.

Of the eight ecological principles, the principle of sustainability, as defined, more or less derives from all the others, and does not exist independently of them. For each of these principles, the editors attempt to derive an analogical principle for business, in order to steer business towards sustainability. This in effect means replacing the push for 'competitive edge' by the push for 'sustainable advantage'. The issues raised in this essay naturally come up for more concrete discussion in some of the other essays.

NGOs have played a very significant role both as pressure groups, and in an investigative capacity, particularly when it impacts upon the clandestine introduction of technologies, and products on unsuspecting populations or users. José Lutzenberger discusses his experiences in Brazil that brought together NGOs, scientists, citizens groups to deal with the whole range

of problems relating to agricultural practices. Undoing the myth that modern agriculture is far more efficient than traditional agriculture, he finds that the former is ecologically pernicious and socially disastrous. His arguments are situated in a perspective opposed to neo-colonialism that works not so much through governments and the military but through transnational corporations and centers of technology development. Thus, what is required in the present world, is not a rejection of modern technology, but an ecological and political critique of it. Deep down however, it appears that Lutzenberger has not come out of the use-abuse model of technology. His own inclination is to examine technologies that work on lines analogous to the closed cycles of nature, and at the broad policy level looks for new ways of integrating the agricultural, industrial, and health sectors.

If NGOs have been playing an important role as a pressure group in gradually bringing the sustainability paradigm into currency, the future of sustainability can be ensured if corporate executives are also convinced of the prevalence of an environmental crisis, and the dire urgency of instituting remedial measures. Kris McDivitt, the former CEO of Patagonia, discusses how she and her colleagues altered the value system of Patagonia. Within the emergent corporate culture, McDivitt is concerned about how a concern for sustainability could be incorporated into industrial practice. Contemporary society is characterized by a proliferation of professional opportunities in the managerial sector, and McDivitt feels that the problem has to be addressed at the level of pedagogy at management school. While recognizing the delusory nature of supplanting an aggressive business education with a more comprehensive notion of sustainability, an intermediate step could be one of finding an appropriate space where new goals could be defined for managers and corporate executives. What is most interesting about this essay is that the author goes on to identify possible modifications of management courses that would interlock with the issues of total sustainability.

How do government's intervene in order to promote a new space for sustainability? Monika Greifahn discusses the unique case of Germany, which is the only country where government has taken an activist role in the adoption of sustainability derived guidelines. This, in no small measure, has to do with the sustained political battle undertaken by the Greens party as well as the long tradition of environmental activism. The activist role envisaged for government derives from a shift in policy perspective, wherein government's must not merely be instruments of enforcement — reducing levels of pollution, or enforcing the installation of catalytic converters by industry. Rather, Greifahn suggests that governments must also consider environmental politics to include preventive measures and provide incentives for the development of new production procedures. However, the ecological modernization of a society is premised upon a culture of high technology based on closed cycle systems. The goal of this program of ecological modernization is the production of future-capable and life-long products rather than the wasteful, obsolescence based economy that we currently propagate. A key policy ingredient in the emergence of these systems is waste policy, that promotes multiple-use systems and is based on a closed-cycle economy law that simultaneously controls the flow of wastes, and requires that substances and products meet certain standards.

Distinguished economists such as Hermann Daly discuss aspects of Ecological Tax Reform; while the question of fiduciary responsibility is taken up by Edward Tasch and Stephen Viederman. But the important question that would bother students of technology is what are the possible technologies of the future and what would be the character of industrial production in the next century. These questions are addressed in the essays by John and Nancy Todd and Gunter Pauli, respectively. Pauli goes onto identify a range of industrial clusters that could emerge in the near future, and it is interesting to make a note of the crucial role to be played by biotechnology in this emerging scenario. The ecological world view within which the new industrialization is to be situated would be guided by the values of conservation, cooperation and partnership — an idea we encountered in the opening essay. However, while Pauli does not in his vision subscribe to the myth of technological neutrality, he does acknowledge his empathy with the diametrically opposite myth that of technological autonomy. The goal then is to transform totalitarian megatechnology into one that is restricted by cultural norms: and the ones that will be the most appropriate are the ones that embody the principles of deep ecology. In terms of concrete engineering this would mean developing industrial clusters characterized by zero-emissions, zero-defects, and zero- inventory.

If most of the essays in the book address the reorganization or restructuring of management practices, business and industrial culture on the deep ecology model, the paper by the Todds does something in reverse. Hitherto technology and industry were founded on the mechanistic paradigm. John and Nancy Todd examine how machines, inanimate production systems, will have to be re- engineered by living systems, that will develop into living machines. These living machines are contained ecosystems that are made up of thousands of species of living organisms. The authors suggest that it should be possible to develop these living machines such that their effectivity is four orders of magnitude greater than that of conventional technologies. We have here a discussion of the structural elements of such living machines, and an elaboration of some candidate machines.

Capra, almost a cult figure now, has over the last two decades played an important role in bringing visibility to the new ecological paradigm. This volume manages to skillfully combine a vision with the concrete issues which go into the realization of elements of this picture. In that sense the volume has been well conceived: given the levels of conflict at which the problem has to be addressed. However, there is one important level of conflict which appears to have been ignored: and this has to do with the tension bound relationship between the North and the South on the one hand. On the other, business in the North has learnt how to shift problematic industries from the developed to the underdeveloped world. And politically, there is the more important problem of the developed world transferring some of the costs of environmental degradation to the developing countries. Lutzenberger's paper raises some of these concerns from the NGO perspective, but as far as all the other dimensions that are touched upon in the volume the third world is all but invisible.

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Image Analysis, Random Fields and Dynamic Monte Carlo Methods — A Mathematical Introduction, Vol. 27, by Gerhard Winkler (Springer-Verleg, Heidelberg) 1996, pp 324, Price: DM 98.00. [ISBN 3540 57069 1 (h b)]

The book provides an introductory exposition of digital image analysis by using mathematical tools. Whereas, image analysis pertains to generating an appraisal of recorded digital image data, image synthesis deals with translation of real scene to the digital image. This later problem is not covered in the text.

A simplistic description of an analysis problem is presented as deterministic or random distortion of 'real scene (x) to 'observed image (y) as $y=f(x)$. As in many other problems, obtaining inverse of f(.) is only rarely straightforward. Though ad hoc, filtering or graduation methods may yield satisfactory result with some loss of information. On the other hand Bayesian approach to the problem works by mixing prior information with data to yield posterior distribution and a suitable decision rule to solve the inverse problem.

The book comprises seventeen chapters and a comprehensive appendix in seven parts. It assumes no previous knowledge of imaging but elementary level of probability and statistics would be beneficial.

Chapter 1 gives an appraisal of the Bayesian approach to imaging. It introduces prior and posterior distribution, Gibbsian form with energy function H(.) for prior, loss function, risk function, and Bayes estimator. Along with two concrete examples on image restoration (bayesian) and boundary extraction, chapter 2 provides an introduction to image distortion and posterior distribution construction. Importance of an appropriate prior is also illustrated for method of aposteriori estimates.

Chapters 3 and 4 are essential for any in-depth insight into image analysis using markov chain and markov random field. Gibbs field, potential and various limit theorems are introduced for later use in the text. Convergence issues in dynamic Monte Carlo methods discussed later in the text will stand to extract from the limit laws in the fourth chapter.

Since underlying space (X) is too large for static methods to sampling from Gibbs field, to obtain minimum mean square estimate (MMS). Dynamic Monte Carlo method of sampling from a feasible markov chain (which converges) is introduced in chapter 5. The computation of Maximum aposteriori estimate (MAP) for Gibbs field is covered in chapter 5 and 6. By incorporating a simple modification in Gibbs sampler in the form of 'inverse temperature, Simulated Annealing and various cooling schedules are covered with illustrations.

Chapter 7 is a generalization of results in chapter 5 in many ways. It contains law of large numbers for simulated annealing algorithm. Metropolis algorithm as an alternative to Gibbs sampler is covered in chapter 8. Its convergence, application to combinatorial problems such as travelling salesman, graph colouring and Metropolis-Hasting of alternative approaches to stochastic relaxation. In contrast to Dobrushins contraction coefficient, use of principal eigenvalues, variance reduction, relaxation techniques in continuous time and space along with a list of latest references are covered in the text. The relaxation algorithms covered in these chapters are sequential.

Chapter 10 covers parallel algorithms for reduction of computational load in the form of partially parallel and synchronous algorithms.

Part IV of the book has two chapters (11 and 12) devoted to texture analysis. The author uses the word texture in the context of natural scenes with repetitive structures. Although not at an introductory level, the two problems of texture segmentation and classification are covered here with simple examples. Part V has two chapters (13 and 14) on parameter estimation by method of maximum likelihood and pseudo likelihood as applied to various problems in image analysis.

Part VI is a supplement on other important applications. Chapter 15 contains a discussion on Neural Networks under the random field framework. Chapter 16 contains various applications opening vistas for other problems. The appendix of the book provides ways for those who are looking for computer implementation of these algorithms.

On the whole, the book contains material suitable for beginners, professionals, and researchers who are looking for rigorous mathematical treatment of image analysis.

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The Contingent Valuation of Environmental Research — Methodological Issues and Research Needs, edited by David J Bjomstad and James R Kahn (Edward Elgar Publishing Ltd, Glos, UK) 1996, pp 320, Price: £ 49.95.
[ISBN 1 85 895 321 5 (h b)]

In the post-UNCED (United Nations Conference on Environment and Development, Rio de Janeiro, 1992) period, better management of environmental resources of a nation has assumed greater importance to realize objectives of Agenda 21. As a corollary to it, a comparative study of cost-benefit of management of environmental resources is required. In this context, 'contingent valuation' (CV) analysis has emerged as a means of measuring values in environmental policy. It is essentially a survey-based "value elicitation" approach seeking to estimate consumers' willingness to pay for better environmental management or greater preservation as compared to estimates obtained through observation of market transactions.

The book under review contains collection of papers examining the current state-of-the-art in the valuation of environmental resources. The volume is result of a workshop where a group of scholars (except one) from American academic institutions have focused upon critically evaluating the contingent valuation methodology and discussed research agenda to improve estimates of environmental resource values. The main theme of this discussion is centered around obtaining economic valuation through survey measurement of consumer preferences. It makes in-depth examination of CV's theoretical foundations, measurement, validation and calibration, and alternatives.

In the near future, it is expected that the demand for environmental resources valuation methodologies and estimates will grow. In this context the crucial choice in environmental policy decisions will rest on costs and benefits of respective policy alternatives. The search for assessing values in different theoretical formulations (e.g. tradable permits, sources, and sinks) for some of the emerging environmental issues will rest upon valuation methodologies, in general, and CV, in particular. Therefore the editors of the book have argued for developing criteria to evaluate alternative methodological choices. They have also emphasized for developing a CV research agenda, which may be significantly influenced by policy needs.

The book is a welcome addition to the growing literature on environmental resource valuation methods. It significantly enhances knowledge concerning efficacy of CV for the purpose. The book will be of great help for those concerned with assessing environmental resources—economists, lawyers, non-governmental organization, and government bodies.

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SCI-TECH UPDATE

Electron emitter research helps slim down computer displays

At the First International Vacuum Electron Sources Conference held at Eindoven during 1-4 July 96 research trends and the promises that lie ahead in electron-emission have been discussed.

Although miniaturization has brought out wonders in computer technology, the CRT used for display of information is still bulky. For applications in lap-tops and avionics display, one solution takes the form of today's flat screen displays which avoid electron beams and rely on glowing liquid crystal (LCD) displays. But again these are not eminently suitable for applications where large screen displays are required. Thus research is focussed upon using very small electron-emitting devices called field emitters which can be fabricated with current nanotechnology methods.

Field Emitter Displays (FEDs) have some disadvantages in that they often require high voltages and provide a fluctuating current that causes a flicker in display. But efforts are on to come out with new materials, fabrication methods, and strategies for improving their behaviour. Meanwhile other researchers are uncovering new applications for field emitters in microscopy, in slimming down the traditional CRT.

In contrast to the thermionic cathodes which use heat to emit and cause flow of electrons, field emitters (FE) rely on electric field to pull out electrons. Most FEs employ arrays of nanotips, small cones of metal, silicon or diamond that emit a stream of electrons into a vacuum. At the Meeting, Michael Geis of the MIT's Lincoln Laboratories in Boston described his experiments in which he used a diamond grit, a form of diamond which has many sharp edges, at a field strength of 5 V. The low voltage which is probably the theoretical minimum, allows the emitter to be directly connected to the controlling semiconductor electronics, which simplifies the assembly. It is observed that electrons in diamond gain energy from the (electric) field and can be emitted with nearly all the energy that the field imparts on them. In fact diamond films are inherently composed of sharp points at the nanometric scale and so there is no need of shaping them into nanotips.

Among other materials tried to deliver precise electron beams, Walter de Heer from the Ecole Polytechnique Federale de Lausanne, graphite was tried in the form of nanotubes. At the meeting he announced a five-fold increase in the emission intensity-enough electrons to drive phosphor screens. Vu Thien Binh of the University of Lyon, reported an ingenious method for crafting a nanotip only one atom wide by using an electric field to pull a heated viscous material such as tungsten into a point. By this method of using a low energy electrons than those presently used in an electron microscope Binh's technique offers a new method for studying molecules without breaking their C-H bonds of biological molecules.

Robert Pressley from Candescent Technologies (formerly Silicon Video Corp) in San Jose, California said that his company expects to manufacture flat-panel displays using FEs.

A team of researchers from Phillips Research Laboratories discussed about a fully working prototype of a flat-panel display that is basically an adaptation of a conventional CRT. This device uses a linear array of common thermionic cathodes mounted in the bottom of a flat tube less than 1 cm thick, with a phosphor screen on one side and supporting struts in the middle. It is believed that this arrangement enables to precisely direct the electrons to the screen [*Science*, **273** (1996) 1173-74]. ❑

DSRM

High-tech tools for textile industry

An example of how research conducted in a government laboratory can be adapted to the needs of an industry is seen in the partnership known as AMTEX which began in 1993 as a collaborative programme among the US Department of Energy and eleven of its national laboratories, and several textile organizations.

The laboratories under DOE (USA) have developed technologies in energy, environmental cleanup and national defence that could be successfully exploited to be used in US textile industry to improve its competitiveness in worldwide markets and create jobs as well by increasing quality, reducing costs, improving responsiveness and production times by reducing the environmental impacts of manufacturing operations.

The contribution of Lawrence Livermore National Laboratory (LLNL) to AMTEX project covers the following five areas: (1) Demand - activated manufacturing architecture; (2) Computer-aided fabric evaluation; (3) Electronically embedded fingerprint through which the information about the various characteristics of the fabrics can be coded in highly miniatured area which will help in inventory management which may eventually replace the barcode; (4) Textile resource conservation; and (5) Rapid cutting of textiles using lasers.

To improve the entire US textile market place, AMTEX envisions a secure, Internet-based information system to link all sectors of the textile supply chain. The amount of secure "demand" data to be transmitted over the Livermore-designed TEXTNET data transfer system is stupendous. Ten thousand retail companies with 100,000 stores, each with 25000 to 1.2 million Stock keeping units, generate 20 billion apparel and household textile purchases annually worth $ 200 billion. That means electronic communication between apparel and textile manufacturers about the demand for 100 million industry stock keeping units per year.

Although several pairs of industry partners have been electronically transferring purchase orders and advance shipment notices for several years over proprietary networks, LLNL is developing TEXNET which incorporates a demand-activated "pull" transfer of data initiated by the client. In this the software is being developed for client authentication which will make possible secure, selective transfer of data among multiple users. That is Brand A manufacturer must not receive information about sales of Brand B. Also because a client is receiving only a portion of the total data available, the bandwidth requirement for data transfer can be made narrower. TEXNET is designed for the real-time exchange of virtually any type of information and may be customized by its users. Using the Internet, information can securely flow in any direction in the textile pipeline.

For the computer aided fabric evaluation, LLNL is adopting real- time image-processing technology which was originally developed to track the path of a bullet as it flies through the air. In this technique, the camera and computer look for flows in patterns being printed on the fabric or in knitted fabrics. The system can not only detect defects in printing or knitting but can also immediately classify the defect and signal the machine operator that a problem exists and how to correct it.

The proprietary system developed at Livemore mounts a high-speed, line-scan camera or series of cameras depending on the fabric's width over the fabric immediately after the last screen. As the first yards of printed fabric roll beneath the cameras, the computer to which the camera is attached digitizes and dynamically learns the printed pattern by creating a model of the repeated pattern. The computer powerful enough to handle the huge amounts of data that the process generates, can then inspect the printing process on line.

As the manufacturing facility's central computer accumulates data from the dedicated computers at the various fabric printers, quality control should improve considerably. Managers will have a record of problems with specific printing machines and with particular operators. [*Sci Technol Rev*, July 1996, pp 20-23]. ❑

DSRM

New reactor using porous wall technology

Studies on a new design of reactor, employing porous wall technology to control reaction speed, indicate lower capital and operating costs than a falling film design as well as reduced pollution.

The reactor developed by SRI International is tested in the laboratory on a difficult exothermic sulphonation process. However, it can be used in many different reactions such as alkylations, halogenations and polymerisations.

SRI developed the reactor to meet the need for better control of exothermic processes and reduce the problems of hot spots and inhomogeneous reactant concentrations. These can result in the production of undesirable by products and excess consumption of raw materials.

With the help of a computer model, SRI designed a porous wall reactor through which one of the reactants

is added progressively throughout the reactor volume. Heat of reaction can be controlled by limiting the quantity of second reactant introduced and by heat exchangers in recycle or interstage lines. Balls inside the reactor tubes give good radial mixing.

The Company has studied the economics of methyl laurate sulphonation in a 23 000 tonne/year plant using the latest falling film technology and the SRI process. The falling film equipment comprised 100 tubes of 1.0 in internal diameter and 15ft long and a 400 BHP compressor. The porous wall reactor contained 189 tubes of 0.625 in internal diameter and 39 in active length contained in an overall shell size of 45 in long and 19 in diameter.

The Company claims the new reactor itself is five times cheaper than a falling film unit. In a retrofit project, equipment costs are in the range of $ 250 000 while overall capital investment in a grass roots plant is reduced by 30 percent. Total product cost is calculated at 79 cent/1b for SRI's reactor compared with 87 cent/1b for the falling film process.

The company is working with the Center for Waste Reduction Technology of the American Institute of Chemical Engineers and Air Products, Eastman Chemical, Monsanto, Olin and Rhone-Poulenc as co-sponsors. After presentation of results from the bench scale trials, each company will decide on the next step to commercialize the process [*Eur Chem News*, 66 (1732) (1996) 31]. ❑

Innovative THF technology

A new low cost clean technology for the production of tetrahydrofuran (THF) from butane will be brought onstream by DuPont by the end of the year, at its Asturias plant in Spain.

The new process contains three important innovations: the use of a circulating fluidised bed (CFB) for partial oxidation of n- butane; attrition-resistant catalyst particles for use in the CFB, and the development of a highly selective catalyst for the hydrogenation of maleic acid to THF.

Butane is converted to maleic anhydride, which is then absorbed in water to form maleic acid. The crude maleic acid is catalytically hydrogenated to THF, which is recovered after extractive distillation.

DuPont says the use of the CFB makes the process superior to fixed-bed and conventional fluidised bed reactors. CFBs are particularly suitable for processes incorporating fast reactions requiring reversible catalysts deactivation, or reactions where an intermediate product is desired.

However, CFBs can cause higher rates of particle attrition. To overcome this DuPont used vanadium phosphorus oxides, normally used for butane oxidation, encapsulated in a microporous silica shell. According to DuPont, these exhibited three times the attrition resistance of commercial fluid catalytic cracking catalysts in standard tests.

The final innovation is the development of a selective catalyst for the hydrogenation of maleic acid to THF, 1,4-butanediol, or to mixtures of the two, according to the conditions within the reactor. The catalyst contains 1-6 percent palladium and 3-6 per cent rhenium by weight, deposited on carbon substrates. The catalysts give a 100 per cent conversion of reactants and DuPont says the ratio of THF to 1,4-butanediol can be controlled easily.

The output of the 45 000 tonne/year Asturias plant will be used to make polymethylene ether glycol (PMTEG) for the production of Spandex fibres and elastomers, at a plant in the Netherlands.

A second new process to convert THF to Terathane (PTMEG) will be used at plants under construction at LaPorte, Texas, and at Ulsan, Korea. The 20 000 tonne/year plant at LaPorte is due onstream in 1997 while the 30 000 tonne/year plant at Ulsan is due onstream by 1998 [*Eur Chem News*, 66 (1739)]. ❑

Kevlar to save lives in the sky

Blastproofing techniques could help prevent aircraft being blown out of the sky by terrorist bombs. The cause of last week's fatal explosion over Long Island, which killed 230 people, is still uncertain. But blast proofing techniques developed by British researchers could protect planes from an explosion, whatever it is caused by test explosions in an aircraft similar to a Jumbo jet have shown that cargo holds reinforced with light, cheap, blastproof materials can with stand three times as much explosive force as unreinforced holds.

As part of a £5-million project jointly funded by the government and the Civil Aviation Authority, The researcher have also devised computer programs to

model the impact of explosions in aircraft. Because of its military research, the agency has copious data on explosives. The Defence Evaluation Research Agency has also carried out extensive research on the properties of aircraft structures and materials.

Explosions will rip the plane apart, even if the initial blast makes only a tiny hole in the fuselage. This is because the pressure of the blast combines with the raised internal pressure of the aircraft to tear a much larger hole. The researchers have looked for ways to prevent holding of the skin and to dissipate the excess pressure from the explosion.

With help from the computer models, the researches selected combinations of blastproof materials that would be cheap and light. Most cargo holds are already lined with plastics based on epoxy or phenolic resins, reinforced with glass fibre. These are designed to survive impacts from dislodged luggage, as well as blocking the spread of fire or toxic gas.

In test explosions aboard a fully pressurised aircraft, found that semi-rigid boards attached to these existing cargo linings made them three times as resistant to rupture. Boards made from Kevlar, a super-tough engineering polymer, cushioned the blast particularly well. The material deforms without breaking, absorbing the pressure as well as the debris of the explosion.

The cost of adding the linings to existing aircraft is minimal. The main penalty as the fuel needed to carry the extra weight around 3 tonnes in a typical Jumbo jet.

Civil Aviation Authority say that despite renewed calls for anti- explosion technology, has no plans to rush through laws requiring blastproofing. Any structural alterations would need to be discussed with aircraft manufacturers and airline operators. ❑

Personal-movie screen

Sony company responsible for providing personal entertainment through Walkman as a portable device, has added a new dimension in coming out with a personal movie screen mounted in a headgear.

The gadget consists of a Liquid Crystal display (LCD) monitor that allows individual viewing of movies and video disks.

Called PLM-50 Glasstron, it features a personal display monitor contained in a special headgear and playback images from a video cassette recorder or a video compact disk (CD) player. It also contains stereo ear phones.

Glasstron measures 20 cm by 12 cm by 26 cm, weighs about 300 g and may be carrying a price tag of about $814.00.

By changing the degree of transparency of the liquid crystal shutter, viewers can enjoy the impression of being in a cinema hall or alternatively, of watching a screen hanging in mid air.

A lithium-ion battery pack is used which may allow 2 hr and 20 min. of continuous playback in a portable setting used with a light-weight CD player. It serves as a portable, individual entertainment device without disturbing those around them. Sony has plans to manufacture about 5000 LCD monitors a month [*Electron Today*, **27** (7) (1996) 44]. ❑

DSRM

SITRA develops hygienic finish for medical cloth

The South India Textile Research Association (SITRA) has developed a hygienic chemical finish for yarns and fabrics to be used for hospital textiles. The new product called 'Santimit' is a synergistic system of chemicals in optimized dosages, capable of resisting bacterial infections.

Santimit can improve tear strength and aesthetic properties of hospital textiles. The bactericidal potentiality of the finish is so effective that it makes the cloth impregnable to almost all major diseases even after fifty washes. The finish can be applied to both woven and knitted fabrics and garments by conventional process involving padding, drying and curing.

Elucidating the feasibility and advantages of the new finish, the researchers say that application of a 10 per cent aqueous solution of it to cotton fabrics enhances the cloth's bactericidal capability along with a rise in tear strength and aesthetic properties. After the padding process, the cloth is dried at 80°C for 10 min and cured at 150°C for 5 min, followed by washing for 10 min to dispense with residual chemicals.

If garments are given a bucket dip in diluted Santimit formulation and air-dried for semi-durable hygiene effect, they would acquire a self-sanitation effect, obviating a lot of washing, sanitisation and sterilization in hospitals.

The bactericidal effect of both the original formulation and the treated materials have been confirmed by extensive hospital field trials. As the finish is composed of non-toxic and non-irritant constituents, it does not cause allergy or discomfort to the users. Dermatological tests conducted on over 100 patients and medical staff have endorsed this.

As a proven anti-bacterial, antifungal and anti-mildew agent, Santimit can also be used as a preservative agent and also as an alternative for pentachlorophenol, which has been banned by the European countries due to its carcinogenic effect (*Express Textile*, 03 October 1996). ❑

HKK

Tiny electronic seal that protects cargo

Researchers at the Encrypta Electronics Ltd, UK, have made a small locking system, the Nanoseal. The device protects loads carried by delivery trucks. Nanoseal can identify when a load has been tempered with.

The concept of using a random number generator to create a seal number was so revolutionary that the firm was able to obtain a patent to protect it, and it now has a wide range of products based on the idea.

Electronic seals offer greater security than the traditional disposable seals, they can be reused with consequent savings on operational costs. The seals have HM Customs and Excise Grade-II approval, the highest level for indicative security, and an audit trail. They are the only seals to be independently certified to BS7480 level for security seals.

The system captures all the data automatically, optimizing delivery systems and achieving significant cost savings for customers. Another small version of the seal is the NanoLock; all seals can be customised by Encrypta, based in Newport Gwent, Wales [*Spectrum*, No. 254 (1996) p. 4]. ❑

HKK

Solar-powered source supplies pure water

Kestrel Solar Technology Ltd, a British company, has developed a device with which a sufficient, safe, clean and potable water can be produced for up to 100 people daily from contaminated sources by the daily output through a portable solar-powered water purifier. This stand-alone Solarwater-5 can be set up easily by one person and will operate for longer durations in remote areas and under harsh conditions.

Four high efficiency solar panels generate power for the system's pump. In bad weather, the system can be connected to a 12V electricity supply, or can be operated manually by a built-in hand pump. An optional outlet filter removes residual iodine from the treated water as a separate stage of filtration. A capacity of 4-6 litre of water/min means that in 6h of sunlight the purifier can produce approx. 2,200 litre of treated water. At an average of 20 litre/d, for drinking, cooking and cleaning purposes, this is sufficient water for grouping of up to 100 people. A water meter is fitted to the unit to monitor throughput. System maintenance is simple, and replaceable cartridges for filtration and disinfection are changed quickly and easily. Cartridge housings are made with tough polypropylene, and all connections are made with PVC fittings approved for potable water.

The Solarwater-5 has the capacity to treat 5000 litre of water between cartridge changes. It weighs 30kg and measures 950 by 420m and is 550m high. The solar panels unfold from the unit's strong, corrosion-proof and easily transportable tubular frame.

For further details contact:

Kestrel Solar Technology Ltd, London SWIV 2PE,UK; Fax: 171 828 5741 [*Spectrum*, No. 254 (1996) p. 2]. ❑

HKK

New process opens way to combined production

Ecologically friendly fuel production is to be boosted by a new oxygenates plant to be set up in Canada.

The plant will be the first to produce commercially both ETBE and MTBE for a Canadian three-company consortium, Alberta BioClean, using barley and butane as feedbacks.

Construction of the plant at Edmonton, Canada, is due to begin in 1997. The plant, which will produce 80,000 tonnes/y of the ethers, will come onstream in early 1999.

The US energy company CalEnergy, grain trading and processing company ConAgra and Canadian firm Kiewit Energy Group are the three project sponsors.

The complex will contain butane isomerisation and dehydrogenation process units, ethanol and methanol manufacturing facilities and dual etherification units for the production of ETBE and MTBE. The output of the plant is likely to be a 50:50 mixture of ethers.

The multiple oxygen production (MOP) technology which is the key to the low-cost, renewable process is owned by BioClean Fuels, which is majority owned by CalEnergy and Kiewit Energy Group. The primary strength of the MOP process lies in its novel method of producing methanol. The process recycles the by-products CO_2 and H_2, from ethanol fermentation and isobutane dehydrogenation, to produce methanol.

The facility will be the first of its kind in the world capable of producing commercial volumes of ETBE, a renewably derived, low volatility gasoline additive. ETBE will enable North American refiners to produce the most environment-friendly gasoline possible [*Eur Chem News*, **66** (No. 1731) (1996) p. 22]. ❑

HKK

Most powerful ultraviolet laser developed

For several years, Prof Mike Key heading the Central Laser Facility at Rutherford Appleton Laboratory near Oxford (UK) have been developing versatile ultraviolet and XUV laser [for a review, see Key, M *J Sci Ind Res*, **50** (1990), 166-73]. Most recently this RAL team developed the most powerful krypton fluoride pulsed laser. It is an unique and unpanalleted development in the world. Known as *Titania*, the new laser system has the capacity to generate powers around 10 terrawatts in a single KrF pulse lasting only for a 300 femtosec and at a wavelength of 249 nm. The laser is expected to be used in several advanced applications, esp in high-energy plasma physics, D-T nuclear fusion, microlithography of semiconductor devices, etc.

Krypton fluoride lasers have an unltra-violet wavelength of 249 nm. The are able to amplify very short pulses and offer a relatively high level of efficiency, converting 5% of 'wallplug' electricity to laser light.

Titania's krypton fluoride pulses, amplified to generate a laser beam 4 cm in diameter, can either be delivered directly to users' experiments or used to power Raman lasers that combine the energy form many KrF pulses and deliver it to a target, but a multi-pulse Raman laser system is to be installed during next year.

According to Prof Key, the new UV laser has immense potential for this powerful research tool. Furthermore, titania will open up new areas of research in the application of extremely high laser intensity for the user of our facilities which include UK universities, the European Union and the United States. [*BCN* (Brit Comm News), Nov./Dec. 1996, 18]. ❑

RS

Laser torch for deep sea inspection

For making sea divers' work safer and quicker, electronic engineers under Dr. Bob Allwood Cranfield University in Britain have developed a novel torch based on laser beams. Use of laser beams instead usual powerful search-light type torches ensures considerably enhanced visibility deep interior of the sea. Generally deep sea divers artificial illumination every 30 m down the sea, because ambient sunlight gets rapidly absorbed. Again switching on white light creates a problem through dispersive attenuation, as if one is moving in dense fog with head/amps on full beam.

Basically, the driver is dazzled by the reflection of his own beam. Particles suspended in the sea—plankton, sand grains and plant material—get in the way of the light and reflect it. This back-scatter reduces what the diver can see. At a depth of 30 metres a diver with a conventional torch can barely see a pipeline eight metres away.

The new system can illuminate objects twice as far away that is 50-70 m. To achieve this he has coupled a laser to a computerized imaging device. The diver directs the laser's thin beam at the area he wants to illuminate.

Two mirrors sweep the beam across the target while just above the laser a video camera synchronized with the mirrors captures the image the laser reveals as it sweeps the target.

The pictures are sent to the surface where software cleans the images and are then fed to a monitor for viewing as a single frame. Up to ten frames a second can be shown possibly in front of the diver's eyes [*New Sci*, **152** (No 2056) (1996), 24]. ❑

RS

From waste product to life saver

Until recently, the umbilical cord was seen as nothing more than a waste product at birth, but its significance as a source of stem cells has now become evident from work carried out in Transplantation Sciences Department, Bristol University in South- west England.

Britain has established a second national cord blood bank to enable increasing supplies of blood taken from the umbilical cord and placenta of newly-born babies to be used for the treatment of leukaemia.

Cord blood has many advantages over bone marrow transplants that are currently one of the most common forms of treatment for leukaemia. Until recently, the umbilical cord was seen as nothing more than a waste product at birth, but its importance as a source of stem cells has now become clear.

The new blood bank is being set up at Southmead Hospital, Bristol, where the university research is also based with joint funding of the UK Leukaemia Research Fund and National Blood Service. Its cord blood donations will come from babies born at the hospital's maternity unit.

It is believed that umbilical cord blood is a readily available source of stem cells, which are the cells from which all blood cells grow. Cord blood is an exciting new source of transplantable stem cells.

Its use gives the faster treatment because donors of the right type of blood can be more readily found than bone marrow, matching problems are fewer and the risk of transmitting dangerous viruses is reduced. There is also a greater possibility of finding donors for patients from ethnic minorities or those with rare tissue types [*Spectrum*, No. **254** (1996) p. 20]. ❑

HKK

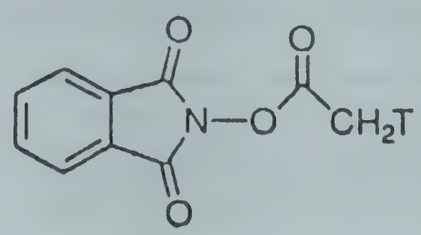
Polymeric resin replaces solvent in 'green' synthesis

Researchers at the Massachusetts Institute of Technology (MIT) have made a polystyrene resin bearing THF side chains that can replace THF as solvent in environment-friendly organic synthesis. Water-soluble THF is hard to recover in industry. S L Buchwald *et al.* dissolved the resin in heptane-toluene and used that mixture as a solvent to carry out an alkylation that usually goes best in THF. Heptane-toluene may be environmentally acceptable under certain circumstances; e.g; if the mixture is to be used in the next step of a multistep sequence or as a recrystallization solvent. The MIT researchers made the THF-functionalized resin by treating *m*-chloromethylstyrene with tetrahydrofurfuryloxymethylstyrene. They polymerized this monomer to a resin that had pendant THF groups[*Chem Eng News*,**74** (38) (1996) p.43]. ❑

HKK

Tritioacetylating reagent labels biological molecules

Manouchehr Saljoughian and his group at the National Tritium Facility, Lawrence Berkeley National Laboratory (LBNL), California, have developed a new reagent to tritioacetylate peptides and other biologically important molecules. Such reagents are needed to radioactively mark many compounds so that their various characteristics and properties can be detected and analyzed. The new compound, *N*-tritioacetoxyphthalimide, has many advantages over standard reagents such as tritiated acetic acid and acetic anhydride.



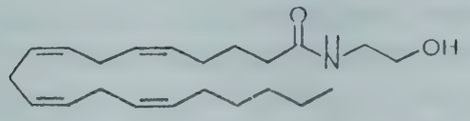
Both substances suffer from low tritium content, volatility, and poor chemical selectivity. Saljoughian *et al.* at LBNL created the new reagent, which readily tritiates α-amino and sulphydryl groups in proteins. *N*-tritioacetoxyphthalimide, which can be easily prepared, is stable and also appears to be active in dimethylsulphoxide, methanol, dioxane, and water [*Chem Eng News*, **74** (38) (1996) p. 43]. ❑

HKK

Chocolate may mimic marijuana in brain

Daniele Piomelli and his colleagues at the Neuroscience Institute, San Diego, have isolated small quantities of *anandamide*, the ethanolamide of arachidonic acid, from chocolate and cocoa powder [*Nature*, **382** (1996) p.677]. The compound is thought to be natural ligand for the cannabinoid receptor, the receptor that binds tetrahydrocannabinol(THC) and is responsible for the high induced by marijuana.

The discovery of *anandamide* in chocolate is unexpected and may be relevant to the well-known "chocolate craving". Prof. Raphael Mechoulam of the Hebrew University, Jerusalem, was the first to discover *anandamide* in pig brain in 1992, naming it from the Sanskrit word "*ananda*", meaning bliss.



Anandamide

Piomelli *et al.* have been studying the formation and inactivation of *anandamide*, searching for leads for drugs to relieve pain and depression.

The pharmacology of chocolate is not yet known. It is difficult to say if it is a food or drug or something in between. *Anandamide* is a fatty acid derivative and chocolate is rich in fats. It is surprising that what makes chocolate so special is tied to the cannabinoid system.

The *anandamide* was found in concentrations of micrograms per gram of chocolate. Much higher amounts of two related compounds: the ethanolamide of oleic acid linoleic acid were also found.

These compounds do not act on the cannabinoid receptor. But they are both fairly potent reversible inhibitors of the enzyme that inactivated *anandamide* by cleaving off the amide group. Thus, these constituents of chocolate may prolong the lifetime of *anandamide* by inhibiting its inactivation.

Piomelli *et al.* are intrigued that these compounds do not act on the cannabinoid receptor. But both are fairly potent reversible inhibitors of the enzyme that inactivates *anandamide* by cleaving off the amide group. Thus, these constituents of chocolate may prolong the lifetime of *anandamide* by inhibiting its inactivation.

The *in vitro* experiments do not address the question of whether *anandamide* ingested as a part of a chocolate bar actually have an effect on the brain.

It is questioned that whether can that chemical get from the stomach to the brain? It is pointed out that the enzyme in the liver most likely would break down the compound first.

There is a lesson to be learned that whether or not the fatty acid amides turn out to be behind the pleasant sensations from chocolate that cause some people to say they are addicted to the stuff. If one can tinker with the endogenous cannabinoid system by inhibiting the inactivation of *anandamide*, and might be able to design drugs that retain the valuable properties of marijuana like analgesia and euphoria, while eliminating undesirable effects like loss of motor control [*Chem Eng News*, **74** (36) (1996) p. 31]. ❑

HKK

Is heart disease programmed before birth?

Researchers at the UK Medical Research Council's (MRC) Epidemiology Unit, Southampton University in Southern England have shown that people who were small at birth are more likely to develop heart disease and high blood pressure in adult life.

These findings have led to the hypothesis that heart disease is 'programmed' by undernutrition and poor growth before birth.

A little is known about the effects of growth during childhood on the risk of heart disease in later adult life, which has led to the collaboration between Southampton University and the National Public Health Institute in Helsinki.

The Anglo-Finnish link-up follows a fruitless search in Britain for records of people whose growth and development has been recorded both at birth and throughout childhood. Such a collection of detailed records has recently been discovered in Finland which are being used for a five-year joint investigation.

The Finnish records contain measurements of children's size at birth as well as information on their height, weight, illnesses and living conditions, collected from child health centres and schools.

Financial grant of £ 400,000 has been provided by the British Heart foundation to study the records of 14,500 men and women born in Helsinki between 1925 and 1939 to note how patterns of growth during infancy, childhood and puberty have modified the risk of developing heart disease in adult life.

Finland has some of the highest rates of heart disease in the world, and therefore it will provide an important setting for this new investigation into the early origins of cardiovascular disease [*Spectrum, Br Sci News*, **No. 254** (1996) p. 18]. ❑

HKK

Microwaves in pest control

A self employed consulting engineer, Halverson in South Central Wisconsin is engaged with the design and in future years, manufacture of a microwave applicator for killing insects in stored grain. At present two entomologists at the ARS Stored Product Insect Research Unit at the University of Wisconsin in Madison are assisting him gather basic research data needed to establish optimum frequencies and temperatures for microwaving grain weevils.

Insects have developed resistance to chemicals used in pesticides. Also the US Environmental Protection Agency is banning a commonly used fumigant, methyl bromide by 2001. In view of this, Halversons's microwave applicator could lead to an alternative to chemicals used to control pests in stored grain and stored-grain products.

In preliminary studies done 2 years ago, Burkholder and Halverson eliminated 94 percent of maize weevils, *Sitoplilus zeamais*, in samples of soft white wheat at a temperature of about 122°F. At 145°F, 100 percent of the insects were killed.

The weevils live as larvae inside grain kernels before they hatch into adults. Maize weevils infest wheat, barley oats, and corn.

The practical application of this research technology will result in equipment that will apply microwave energy to the grain as it flows continuously from bucket elevators and into storage facilities.

Halverson will begin his design with information gathered from latest experiments at the OINL in Oak Ridge, Tennessee. Later patent may also be field for his design. By using higher microwaving frequencies it take less time to kill insects. The cost of microwaving at the prevalent energy prices, including capital equipment, operating, and fixed costs, works out to be comparable to that of chemical treatment methods [*Agr Res*, **44** (5) (1996) 21]. ❑

DSRM

Novel method to dump carbon dioxide generated from power stations

Any effort to reduce the global warming in the various operations in any field are greeted well. As another contribution to solution of this environmental problem, British Geological Survey (BGC) believes that they have found a solution to the problem of containing all the CO_2 that is emitted from oil and gas fired power stations. Their suggested solution: pump the gas back into the deep underground rock from which the oil and gas come in the first place.

Out of the options available to the BGS Scientists, one was the deep ocean dumping. But it was ruled out in view of the distance and costs involved in transporting the gases to sites in the Central Allantic. Absorbing the gas biologically using trees and foliage or disposing of the CO_2 underground in old mine workings etc. have been considered but were found to be impractical.

The BGS scientists working with an international team drawn from other research organizations, and oil and gas companies used the option of using the rocks beneath the North Sea as a reservoir for the Waste CO_2. The CO_2 is extracted from the flue gases of the power stations, compressed to a super critical fluid and piped to the disposable area. From there it is pumped into the permeable rocks.

It is believed that the gas will slowly dissolve and react with the water in the pore spaces of reservoir rocks and with rock itself. It is estimated that the storage will be assured for at least tens of thousands of years. However, the cost factor has to be worked out.

But meanwhile, Statoil — the Norwegian state oil and gas company is going ahead with pumping CO_2 into rocks deep under the North Sea. The company will strip CO_2 directly from the gas (rather than at power stations), compress it and then pump it back into the rock that held the gas. BGS have plans to study the fate of CO_2 thus pumped into the rocks through another project [*Chem Brit*, **32** (9) (1996) 9]. ❑

DSRM

Gel revitalises men

A Gel that stimulates an erection when rubbed on the penis could provide new hope for impotent men. The gel is being tested on 75 impotent men and results are expected by the end of the year.

If the gel works, it could replace more invasive treatments, such as inflatable penile implants and injections. The gel is applied directly to the penis 15 to 20 minutes before intercourse explains MacroChemm the company in Lexington, Massachusetts that developed the substance.

Like some other treatments for impotence, the gel relies on the action of the hormone prostaglandin E1. This substance relaxes smooth muscle in the arteries of the penis and the corpus cavernosum, the main channel the engorges with blood during an erection. Only if the muscle is relaxed will blood remain in the penis, sustaining an erection.

Existing prostaglandin treatments are invasive. Men inject the hormone directly into the penis, or insert a pellet two or three centimetres down the urethra. MacroChem's gel contains 2-n-nonyl- 1,3-dioxalane, which temporarily opens channels through the outermost layer of the skin. This allows prostaglandin in the gel to diffuse into the penis. A senior urologist at the Middlesex Hospital in London feels that although the gel might work he is concerned that prostaglandin deposited in the vagina of a pregnant woman during intercourse could cause a miscarriage by triggering contractions. Macro Chem is confident this would not happen, because the dose is so small [*New Sci*, 151 (2040) (1996) 187]. ❑

Repairing kidney with osteogenic protein

Ratse with severely damaged kidneys can be restored to health with a protein already used to repair bones, cartilage and eye tissue. This versatile substance, called osteogenic protein-1 (OP-1), helped the animals' kidneys recover whether they had been damaged suddenly through acute renal failure, or progressively through chronic kidney disease.

Creative BioMolecules, the company developing the protein in Hopkinton, Massachusetts, hopes that it will reverse chronic kidney damage in people who at present have to rely on dialysis machines. The company also expects OP-1 to save people who might otherwise die from kidney failure following heart attacks, accidents and other traumatic events in which the blood supply to the kidney is interrupted. No reliable treatment exists for kidney conditions, and a million people around the world depend on dialysis machines.

At a conference in Washington DC, the company and its academic associates described their success in using OP-1 to treat acute kidney failure in rats. Typically, a third of the control animals died, whereas all the animals injected with the protein survived.

Joe Bonventre and his colleagues at Harvard Medical School showed that concentrations of waste products such as creatinine and urea, which accumulate in damaged kidneys, returned to normal in the organs of animals receiving the protein.

In the acute kidney failure that follows trauma, most of the damage occurs when the blood supply to the organ resumes. White Blood cells called macrophages flood into kidney tubules and begin destroying tissue. While the reasons for this are not entirely understood, Creative BioMolecules suggests that macrophages may be "cleaning up" oxygen-deprived cells that they see as defective, even though the cells could recover.

The protein seems to interfere with the ability of macrophages to attach to the walls of the tubules, If the macrophages are kept at bay, kidney cells survive and the organ recovers.

Results have been equally encouraging in rat experiments that mimic chronic kidney disease. Untreated animals usually die after three months, but the treated animals live on.

Earlier experiments have already indicated that OP-1 plays an important part in kidney growth. These experiments knocked out the gene for making OP-1 before the animals were born. The rats hardly developed kidneys at all, and most of them died after 10 days or so.

Testing of OP-1 for human bone and cartilage repair is already well advanced. The protein acts on primitive cells from the bone marrow called stem cells, instructing them to become different types of cells in all kinds of damaged tissue, where they tend to accumulate [*New Sci*, 150 (2031) (1996) 25]. ❑

Ethylene/styrene plastic

Dow Chemical has demonstrated that it is possible to copolymerise ethylene and styrene with a metallocene catalyst to produce a new range of plastics. The polymers have been named ethylene-styrene interpolymers (ESIs) and Dow claims that they will be of 'significant commercial interest'.

Copolymers with up to 80 per cent by weight of styrene have been produced in a solution process using constrained geometry catalysts from Dow's Inside technology.

The molecular weights of the copolymers vary from 10 000 to 500 000 with distributions in the range of two to three. Dow has produced alternating and pseudorandom copylymers by altering catalyst structure and selection.

The new polymers will find applications in packaging, general durables, wire and cable, toys, automotive parts, general elastomers, gaskets and profiles [*Eur Chem News*, **66** (1739) 23]. ❑

Improved maleic anhydride production

Improved catalysts for maleic anhydride production are under development at the Leverhulme Centre for Innovative Catalysis at LIverpool University in the UK.

Researchers have been able to produce vanadium phosphate catalysts with greatly enhanced surface area, resulting in higher MA output and lower levels of carbon monoxide and dioxide by products.

The Centre and its partner in France, the Institut de Recherches sur la Catalyse, is also looking at a novel vanadium phosphate structure that has high selectivity for MA and virtually no carbon oxide byproducts, although conversion rates are currently low.

The key to both developments is in the use of water and alcohol in the use of water and alcohol in the catalyst production. Commercially used catalysts are made by reacting vanadium pentoxide with phosphoric acid in alcohol (a reducing agent) to give vanadium phosphate hemi-hydrate. An alternative two-step process was develop by Exxon in the late 1980s in which the pentoxide is reacted with the acid in water, to give the dihydrate, and then reduced in alcohol to the hemihydrate.

The Liverpool advances have been made using this process, varying the alcohol used and going to higher carbon numbers. By using a primary alcohol instead of the conventionally used secondary alcohol, the catalyst surface has a rose-like structure instead of the usual flat platelets. Each rose is only 1 μm across and contains numerous petals, giving a surface area of over $40m^2/g$ of catalyst compared with industrially used materials with $15\text{-}20m^2/g$. The result is a doubling of MA production, and a reduction of 15 per cent in carbon oxides. It has also been found that by using 3-octanol, a catalyst can be made with a vanadium: phosphate ratio of 2:1 (rather than the conventional 1:1) with a very high specificity to MA. Further development is being sponsored by the UK government under its clean technology initiative [*Eur Chem News*, **66** (1732) (1996) 31]. ❑

Honours and Awards

Prof Amir Pnueli awarded 1996 Turing Award

Prof. Amir Pnueli, a Weizmann Institute of Science mathematician has been named the recipient of the 1996 Turing Award, the world's most prestigious prize, dubbed as the "Nobel Prize in computer science." The A M Turing Award is named after Alan M Turing (1912-1954), the Scottish mathematician considered to be among the fathers of modern computer science. The Award is granted annually by the Association for Computing Machinery for major and lasting contributions to the computing community. Pnueli's innovtive approach, first published in 1977, introduced temporal logic into computer science as the appropriate language for specifying and verifying reactive programs.

Pnueli is responsible for the introduction of a number of new concepts, computational models and verification methodologies that have been adopted by the entire scientific community dealing with system verification. For example, he characterized the class of reactive systems as systems whose role is to maintain an ongoing interaction with their environment, rather than compute a final result. He argued that such systems are particularly difficult to program correctly, and showed that temporal logic is the right tool for their specification and verification.

An important extension to the temporal methodology was Pnueli's development of real-time temporal logic, which makes possible the precise analysis of real-time systems whose reliability is dependent on

their ability to react to external stimuli within particularly short time periods.

Another concept recently developed by Pnueli is that of hybrid systems. For many years, it was common to distinguish between discrete components (such as a digital controller that decides on the opening and closing of valves) and continuous ones (such as the chemical and physical processes themselves). A system that controls a production line in a large factory naturally includes both discrete and continuous components. Pnueli found a way to combine these components into the single mathematical model of hybrid systems which can be specified and verified by temporal technology.

Pnueli is personally involved in numerous research projects at various international institutions. Born in Nahalal, Israel, Pnueli received his Ph.D. at the Weizmann Institute and then conducted research at Stanford University in the U.S. He founded and headed the Department of Computer Science at Tel Aviv University before returning to the Weizmann Institute in 1980 [*Weizmann Inst Sci News*, November 7, 1996]

❑

DSRM

Journal of Scientific & Industrial Research
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Instructions to Contributors

The **Journal of Scientific & Industrial Research** (Incorporating *Research and Industry*) is published monthly to serve as an information link between the generators and users of technologies. It is addressed primarily to industrial entrepreneurs, technologists, engineers, technocrats and administrators in industry. Therefore, original research articles of practical interest to industry are invited for publication.

Contributions should have an economic bias, and wherever possible, cost estimates should be provided. They should be tersely written, giving only the significant results.

Besides, reviews on various branches of science and technology, science/industrial policy and management are also accepted.

Subject Coverage

Scientific Industrial Research

(i)Scientific investigations successful at the pilot-plant and in-plant trials.

(ii)Technology upgradation.

(iii)Development of cheaper and indigenous raw materials as replacement for uneconomical materials.

(iiv)Import substitution.

(v)Technologies for rural development.

(vi)Standardization and quality control.

(vii)Technologies of waste management.

(viii) Industrial R&D highlights.

Technology Management

(i)Success/failure stories in technology management.

(ii)Technology assessment.

(iii)Technology transfer.

(iv)Technology assimilation and adaption in different industries.

(v)Technology funding including venture capital.

(vi)Human Resource Development.

vii)Management.

(viii) Environmental management.

Industrial Development

(i)Policies, programmes and progress.

(ii)Critical profiles of industries—individual and sectoral.

(iii)Technology Forecasting .

(iv)International Collaboration.

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Questions on the articles published in the journal, answers supplementing any of the published items, views, opinions, or suggestions on the various aspects of technology are welcome for inclusion in the column, 'readers react'.

The editors are keen in projecting the technology bottlenecks/problems faced by the industry for their solution by the scientists in various laboratories. They would welcome to be mediators between the industry and the laboratory.

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In citing ***references to research papers***, names and initials of the authors should be followed, in order, by the title of the periodical in the abbreviated form (italics), the volume number (bold), the year within circular brackets and the first page reference ,e.g. Liotta R, Rose K & Hippo'E, *J Org Chem*, **46** (1981) 227.

For names of periodicals, the standard abbreviations listed in the *International Serials Catalogue* published by the International Council of Scientific Union's Abstracting Board should be used. If the reference is to an article published without any

authorship in a periodical, the title of the artilce takes the place of the author in the citation, e.g. Handloom Sector of Textile Industry in India, *J Mater Sci*, **18** (1983) 1443.

If a paper has been accepted for publication, the names and initials of the authors and the journal title should be given followed by the words "in press" within circular brackets, e.g. Chavan R B & Subramanian A, *J Sci Ind Res*, (in press).

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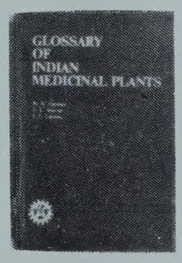

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